

SOME INORGANIC AND ORGANOMETALLIC CHEMISTRY
OF PALLADIUM(II) WITH PYRIDINE BASED LIGANDS

by

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This thesis contains no material which has been accepted for the award of any other degree or diploma in any University, and to the best of my knowledge, contains no copy or paraphrase of material previously presented by another person, except where due reference is made in the text.

Nigel J. Minchin.

spelling and expression.

Financial support from the Commonwealth of Australia for the provision of a Postgraduate Research Award, is gratefully acknowledged.

FOR MY FAMILIES OF
BLOOD AND SPIRIT.

Abstract

This thesis describes the results of a study of inorganic and organometallic chemistry of palladium(II) with 2- and 2,6-disubstituted pyridine containing N-donor ligands. Ligands of this type have been used to assess the ability of palladium(II) to adopt coordination geometries higher than the characteristic square-planar geometry, to determine whether palladium(II) substrates will undergo metallation reactions with polydentate pyridine donor ligands, and to synthesise complexes in which palladium(II) is bound to carbon atoms of the ligands at sites other than those expected via cyclometallation reactions.

Inorganic complexes derived from the reaction of ligands, L, with palladium(II) acetate and chloride substrates have allowed the isolation of complexes of the form $[L_nPdX_2]$ (where $X = OAc, Cl$; $n = 1$ (polydentate), $n = 2$ (unidentate)), $[LPdX]X$ ($L =$ planar tridentate; $X = OAc, Cl$), $[L_2Pd]X_2$ ($L =$ tris(pyridin-2-yl)methane; $X = NO_3^-$), and the related poly(pyrazol-1-yl) complexes $[(pz_3CH)_2Pd]X_2$ ($X = NO_3^-, BF_4^-, ClO_4^-$), and $[(pz_3BH)_2Pd]$. X-Ray structural analyses show that $[(pz_3BH)_2Pd]$ and the cations $[L_2Pd]^{2+}$ ($L =$ tris(pyridin-2-yl)methane, tris(pyrazol-1-yl)methane) have square planar coordination with two uncoordinated donor groups. An X-ray structural determination of the complex $[LPd(OAc)](OAc) \cdot 3H_2O$ (where $L =$ the 2,6-disubstituted pyridine ligand *meso*-(pyPhMeC) $_2C_5H_3N$) has been obtained confirming the planar tridentate nature of the ligand and presence of a unidentate acetate group.

In conjunction with the investigation of the coordination preferences of palladium(II), the coordination properties of the new ligand (pyPhMeC) $_2C_5H_3N$, have also been assessed by the formation of methylmercury(II) nitrate complexes. Fractional crystallisation has allowed the separation of *meso* and *racemic* forms of the complex, and further reaction with sodium cyanide has afforded the free ligand separated into its *meso* and *racemic* diastereoisomers. An X-ray structural study has shown that the *meso* complex is four-coordinate and contains the ligand as a tripodal tridentate. Thus, the *meso* form of the ligand has been

shown to exhibit two binding modes, planar-tridentate to palladium(II), and tripodal-tridentate to methylmercury(II).

Attempted cyclopalladation reactions of the ligands py_2CH_2 , $\text{py}_n\text{Ph}_{3-n}\text{CH}$ ($n = 1-3$), and py_3PhC , with palladium(II) acetate in glacial acetic acid has resulted in the isolation of a dinuclear (*C,M*)-cyclopalladated product of pyPh_2CH ; dinuclear chloro- and mononuclear acetylacetonato-complexes have also been prepared to assist with spectral characterisation. The remaining ligands studied form bidentate chelate complexes, $[\text{LPd}(\text{OAc})_2]$, with no evidence of metallation products.

Similar reactions using meta-disubstituted benzenes, for example, $(\text{pyMeHC})_2\text{C}_6\text{H}_4$, have resulted in metallation of the central benzene ring to give mononuclear (*N,C,M*) complexes, for example, $[(\text{pyMeHC})_2\text{C}_6\text{H}_3]\text{Pd}(\text{OAc})$.

In contrast to palladation of pyPhCH_2 and pyPh_2CH , which occurs at the ortho-position of a phenyl ring, lithiation of these and related pyridines such as py_2CH_2 occurs at the bridging carbon atom to give the salts $\text{pyR}_1\text{R}_2\text{C}^-\text{Li}^+$ (where R_1 and R_2 are hydrogen, phenyl, or pyridin-2-yl substituents). Organolithium derivatives of these ligands have been used in attempts to synthesise organopalladium(II) complexes in which palladium is bound to the bridging carbon atom, and to synthesise organomercury(II) reagents for possible use in synthesis of organopalladium(II) complexes. Thus, investigation of the reaction of the anions pyMe_2C^- , $\text{py}_n\text{Ph}_{2-n}\text{RC}^-$ ($\text{R} = \text{H, Me; } n = 1, 2$), and $\text{py}_n\text{Ph}_{3-n}\text{C}^-$ ($n = 1-3$), with mercuric iodide have been performed in an attempt to obtain diorganomercurial reagents, $[\text{R}_2\text{Hg}]$. The reactions have resulted in the isolation of oxidative coupling products $(\text{pyMe}_2\text{C})_2$, $(\text{py}_n\text{Ph}_{2-n}\text{RC})_2$ ($n = 1, 2; \text{R} = \text{H, Me}$), and polymeric products for the triarylmethanes, respectively. Similar reactions with Ph_2CH^- and Ph_3CH^- have resulted in isolation of $(\text{Ph}_2\text{HC})_2$ and triphenylmethylperoxide, respectively. Isolation of oxidative coupling products and triphenylmethylperoxide has been explained in terms of decomposition of transient $[\text{R}_2\text{Hg}]$ species. The coordination properties of two dimers, $(\text{pyPhHC})_2$ and $(\text{py}_2\text{HC})_2$, have been investigated by

preparation of their palladium(II) acetate complexes. In the former case selective crystallisation of the mononuclear *racemic* complex was observed, while in the latter case a bridged dinuclear complex $[(py_2HC)_2Pd(OAc)_2]_2$ was obtained.

The ligand anions $py_nPh_{2-n}HC^-$ ($n = 1, 2$) have been reacted with *trans*-(4-methylpyridine) $_2PdCl_2$, $[(\gamma-pic)_2PdCl_2]$. For $n = 1$ a number of products have been obtained and two organometallic dinuclear complexes have been isolated and structurally characterised. One complex has the formulation *trans*-(N, N')- $\{[(\mu-py-M)(PhHC-C)\{(\gamma-pic-M)PdCl\}]_2 \cdot CH_2Cl_2$, with square-planar coordination geometry and two bridging $[pyPhHC-C, M]^-$ groups. For $n = 2$, reaction under similar conditions resulted in the isolation of decomposition products including traces of the ligand oxidative coupling product $(py_2HC)_2$.

As an alternative route to synthesis of organopalladium(II) complexes with palladium bonded to bridging carbon atoms, oxidative addition reactions of $py_nPh_{3-n}CCl$ ($n = 1-3$) with bis(dibenzylideneacetone)palladium(0), $[(dba)_2Pd]$, have been studied resulting in isolation of palladium(II) complexes for $n = 1$ and 2, but not for $n = 3$. For $n = 1$ a chloro-bridged dinuclear allylic complex, similar to the oxidative addition product formed between triphenylmethylchloride and $[(dba)_2Pd]$, has been obtained. For $n = 2$ a dinuclear complex has been obtained and structurally characterised. The complex has a formulation *trans*-(N, N')- $\{[(\mu-py-M)(py-N')(PhC-C)\{PdCl\}]_2 \cdot [(CH_3)_2CO \cdot CH_2Cl_2]_{0.5}$ with the ligand $[py_2PhC-C, N, N']^-$ σ -bound to palladium *via* the bridging carbon atom. In each ligand one pyridine N-donor bridges two palladium atoms while the second forms a four-membered (C, N)-chelate ring to the supporting palladium atom.

Methods for the synthesis of pyridine-based ligands, including the preparation of a number of new ligands, are presented.

CONTENTS

	Page
<u>CHAPTER ONE:</u> <u>Introduction</u>	1
 <u>CHAPTER TWO:</u> <u>Inorganic Complexes of Palladium(II) with Pyridine</u> <u>N-Donor Ligands</u>	
2.1 Introduction	13
2.2 Coordination Complexes of Palladium(II) Acetate with Simple Ligands	18
2.3 Coordination Complexes of Palladium(II) Chloride with Simple Ligands	24
2.4 Coordination Complexes of Palladium(II) Acetate with Extended Ligands	27
2.4 (i) Preparation and Characterisation of the Complexes [LPd(OAc)](OAc) (L = planar tridentate)	28
2.4 (ii) The Solid State Structure of <i>Meso</i> -[[(pyPhMeC) ₂ C ₅ H ₃ N]Pd(OAc)] (OAc).3H ₂ O	30
2.4 (iii) Solution Structures of the Complexes	31
2.5 Synthesis and Structural Studies of Palladium(II) Complexes of Tripodal N-donors	46
2.5 (i) ¹ H Nmr Characterisation of the Complex [(py ₃ CH) ₂ Pd](NO ₃) ₂	48
2.5 (ii) ¹ H Nmr Characterisation of the Complexes [(pz ₃ CH) ₂ Pd](NO ₃) ₂ and [(pz ₃ BH) ₂ Pd]	49
2.5 (iii) Solid State Structures of [(py ₃ CH) ₂ Pd](NO ₃) ₂ , [(pz ₃ CH) ₂ Pd](BF ₄) ₂ , and [(pz ₃ BH) ₂ Pd]	50
2.6 Conclusions	53
 <u>CHAPTER THREE</u> <u>Some Cyclopalladation Reactions of Simple and Extended</u> <u>Ligands with Palladium(II) Acetate</u>	
3.1 Introduction	57

3.2	Simple Ligands	60
3.3	Extended Ligands	62
3.3 (i)	^1H Nmr Characterisation of $[(\text{pyMeHC})_2\text{C}_6\text{H}_3]\text{PdX}$, where X = OAc and Cl	63
3.3 (ii)	The COSY spectrum of $[(\text{pyMeHC})_2\text{C}_6\text{H}_3]\text{Pd}(\text{OAc})$	71
3.3 (iii)	The Solid State Structure of <i>Meso</i> - $[(\text{pyMeHC})_2\text{C}_6\text{H}_3]\text{Pd}(\text{OAc})$	74
3.3 (iv)	Cyclometallation of an Extended Ketone, $(\text{pyOC})_2\text{C}_6\text{H}_4$	76
3.3 (v)	The Solid State Structure of $[(\text{pyOC})_2\text{C}_6\text{H}_3]\text{Pd}(\text{OAc})$	77
3.4	Conclusions	81

CHAPTER FOUR: Diastereoisomer Separation using Methylmercury(II) Nitrate Salts

4.1	Introduction	85
4.2	Synthesis and Characterisation of <i>Meso/Rac</i> -($\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}, \text{L}$, and <i>Meso</i> - and <i>Rac</i> - $[\text{LHgMe}](\text{NO}_3)$ Complexes	87
4.3	Solid State Structure of <i>Meso</i> - $[\text{LHgMe}](\text{NO}_3) \cdot 2\text{H}_2\text{O}$. .	88
4.4	Structure of the Complexes in Methanol and Isolation of <i>Meso</i> -L and <i>Rac</i> -L	90
4.5	Conclusions	91

CHAPTER FIVE: The Interaction of Simple Ligand Anions with Mercuric Iodide

5.1	Introduction	93
5.2	Synthesis of Poly(pyridin-2-yl)ethanes and Related Dimers	95
5.3	Characterisation of Poly(pyridin-2-yl)ethane Dimers and some Palladium(II) Acetate Derivatives	99
5.3 (i)	The COSY Spectrum of <i>Rac</i> - $[(\text{pyPhHC})_2\text{Pd}(\text{OAc})_2]$	102
5.4	Conclusions	102

CHAPTER SIX: Preparation of Some Organopalladium(II) Complexes

6.1	Introduction	108
6.2	The Reaction Between Lithiated Ligands and a Palladium(II) Chloride Substrate	112
6.2 (i)	The Solid State Structure of [[$(\mu\text{-py-}M)(\text{PhHC-C})\{\gamma\text{-pic-}M\text{PdCl}\}_2\cdot\text{CH}_2\text{Cl}_2$, Complex (B)	115
6.2 (ii)	Nmr Characterisation of Complex (B) . . .	118
6.2 (iii)	Solid State and Solution Structure of [[$\text{pyPhC:C(Me)O-}N,O\}_2\text{Pd}$], Complex (C) . . .	119
6.2 (iv)	The Structures of Complex D, and [[$(\mu\text{-py-}M)(\text{PhHC-C})\{\text{pyPhCH}_2\text{-}M\text{PdCl}\}_2$, Complex E	123
6.3	The Oxidative Addition of pyPh_2CCl to Palladium(0) .	130
6.3 (i)	Nmr Characterisation of $[(\text{pyPh}_2\text{C})\text{PdCl}]_2$.	130
6.4	The Oxidative Addition of py_2PhCCl to Palladium(0) .	139
6.4 (i)	The Solid State Structure of [[$(\mu\text{-py-}M)(\text{py-}M)(\text{PhC-C})\{\text{PdCl}\}_2$. [[$(\text{CH}_3)_2\text{CO}\cdot\text{CH}_2\text{Cl}_2$]] $_{0.5}$	140
6.4 (ii)	Nmr Characterisation	144
6.5	Attempted Oxidative Addition of py_3CCl to Palladium(0)	149
6.6	Conclusions	149

CHAPTER SEVEN: Ligand Synthesis

7.1	Pyridine and its Effects on Ring Substituents . . .	153
7.2	Starting Materials	154
7.3	Ligands Containing One Bridging Carbon Atom: "Simple Ligands"	156
7.4	Ligands Containing Two Bridging Carbon Atoms: "Extended Ligands"	159
7.4 (i)	Extended Ligands Linked by a Pyridine Nucleus	160
7.4 (ii)	Extended Ligands Linked by a Benzene Nucleus	162

CHAPTER EIGHT: Experimental

General	168
Palladium Recovery and Starting Materials	172
Complexes of Palladium(II) Acetate	175
Complexes of Palladium(II) Chloride.	181
Palladium(II) Cationic and Neutral Complexes of the type $[L_2Pd](X)_2$ and $[L_2Pd]$	184
Cyclometallation Products from Palladium(II) Acetate.	187
Methylmercury(II) Nitrate Complexes of $(pyPhMeC)_2C_5H_3N$	191
Ligand Dimerisation using Mercury(II) Iodide	193
The Reaction Between Lithiated 2-Benzylpyridine and <i>trans</i> -{bis(4-methylpyridine)}palladium(II) chloride .	197
Oxidative Addition Reactions with Bis(dibenzylideneacetone)palladium(0)	201
(Pyridin-2-yl)methane Ligands and Derivatives	204
Extended Ligands Containing Two Bridging Carbon Atoms	209
<u>PUBLICATIONS.</u>	220

ORTEP Diagrams of New Structurally Characterised Complexes

page

Inorganic Palladium(II)

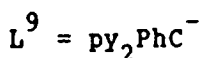
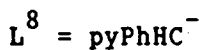
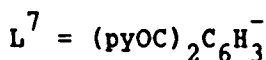
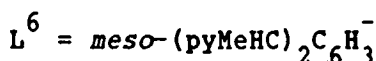
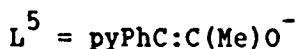
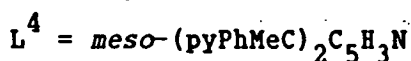
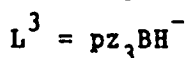
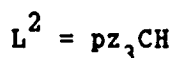
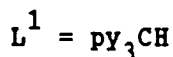
$[L_2^1 Pd](NO_3)_2$	51
$[L_2^2 Pd](BF_4)_2$	52
$[L_2^3 Pd]$	52
$[L_2^4 Pd(OAc)](OAc)$	30
$[L_2^5 Pd]$	122

Methylmercury(II) Nitrate

$[L^4 HgMe]NO_3$	89
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Organopalladium(II)

$[L^6 Pd(OAc)](Pd-C(aryl))$	75
$[L^7 Pd(OAc)](Pd-C(aryl))$	79
$[L^8 (\gamma-pic) PdCl]_2(Pd-C(alkyl))$	116
$[L^8 (L_{+H}^8) PdCl]_2(Pd-C(alkyl))$	129
$[L^9 PdCl]_2(Pd-C(alkyl))$	142



Commonly used Abbreviations

acac	deprotonated 2,4-pentanedione
bpy	2,2'-bipyridyl
COSY	^1H correlation spectroscopy (J-coupled)
DEPT	distortionless enhancement by polarisation transfer
dba	dibenzylideneacetone
L	Ligand (mono-, bi-, and tridentate)
R	alkyl or aryl group
Me	methyl group
Mim	N-methyl(imidazol-1-yl) group
OAc	acetate (anion)
Ph	phenyl group (C_6H_5)
PhCN	benzonitrile
γ -pic	γ -picoline, 4-methylpyridine
py	pyridine, or pyridin-2-yl substituent
pz	pyrazol-1-yl substituent
THF	tetrahydrofuran
X	anion, usually halide or acetate
Y,Z	C-H group or heteroatom (usually nitrogen)
α	sp^3 atom of a substituted 2-methylpyridine moiety
η^3	azaallylic or benzylallylic ligand
μ	bridging group
ν_{as}	asymmetric vibrational mode (carboxylate)
ν_{s}	symmetric vibrational mode (carboxylate)

CHAPTER ONE

INTRODUCTION

Palladium possesses properties typical of the platinum group metals, and has a chemistry dominated by oxidation states (0) and (II) with d^{10} and d^8 electronic configurations, respectively.

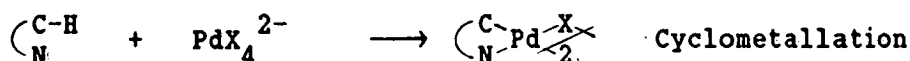
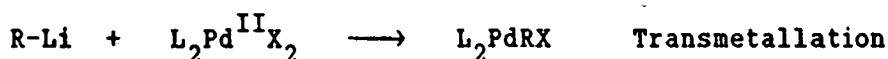
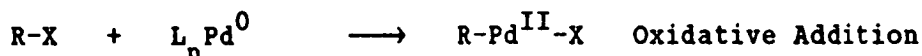
In its zerovalent state four-coordinate geometry is most common, for example, $[(Ph_3D)_4Pd]$ (where $D = P, As, Sb$)¹⁻³, and $[(COD)_2Pd]$ (where $COD = 1,5$ -cyclooctadiene)⁴, although coordinatively unsaturated species may also be isolated, and are believed to be active participants in many catalytic systems. Three-coordinate $Pd(0)$ species are typically of trigonal geometry and this has been demonstrated for the synthetically important complexes $[(dba)_3Pd]$ ⁵ and $[(dba)_3(solv.)Pd_2]$ ⁶ (where $dba =$ dibenzylideneacetone and $solv. = CHCl_3, CH_2Cl_2, C_6H_6$). Two coordinate complexes have also been suggested in phosphine dissociation from $[(R_3P)_4Pd]$ in organic solvents⁷ and have been structurally characterised in complexes of the type $[(t-Bu)_2PhP]_2M$ (where $M = Pd, Pt$)⁸.

Similarly, for complexes of palladium(II), examples of square-planar geometry are abundant. However, for palladium(II), enlargement of the coordination sphere in the solution state often occurs and is invoked in explaining exchange mechanisms⁹ and catalytic properties of such complexes. The question of stereochemistry and fluxional behaviour in five-coordinate transition metal complexes has been of continuing interest. Pentakisphosphite complexes of the form $[(RO)_3P]_5M^{2+}$ (where $M = Co(I), Rh(I), Ir(I), Ni(II), Pd(II)$ and $Pt(II)$) have been prepared and have been shown to be trigonal-bipyramidal in solution at low temperatures.¹⁰ Fluxional motion occurs at higher temperatures making all ligand environments equivalent.

In the solid state, higher coordination has been suggested for some complexes, for example, $[(tasol)PdX_2]$ (where $tasol =$ bis(3-dimethylarsinopropyl)but-3-enylarsine).¹¹ However, X-ray structural analyses of five-coordinate palladium complexes are few in comparison to other platinum group metals. Reaction

between bis(hexafluoroacetylaceto)M(II) (M = Pd, Pt) with tri-o-tolylphosphine has provided complexes giving proof of higher coordination in the solid state.¹²

Organopalladium(II) σ -complexes, derived from a variety of sources including oxidative addition (Pd(0) substrates), transmetallation (Pd(0) and Pd(II)), or cyclometallation (Pd(II)), are of increasing importance as intermediates in synthetic organic chemistry.^{13,14}



The propensity of the Pd-C σ -bond to insert unsaturated molecules is fundamental to many of these syntheses. For organic synthesis employing the cyclometallation reaction, the effect on stability of the Pd-C σ -bond conferred by ancillary donor ligands is of particular concern in the design and action of such reaction intermediates. For catalytic activity, involving oxidative addition and transmetallation reactions as part of the catalytic cycle, the formation of transient σ -organopalladium species is required, while in stoichiometric reactions stable σ -bound complexes are frequently preferred.

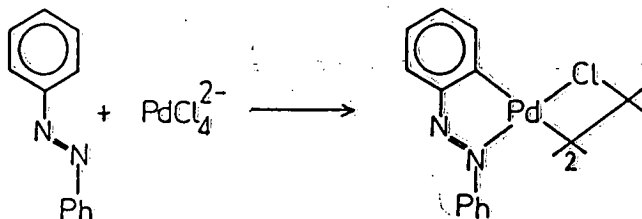
The precursors for the formation of inorganic and organometallic complexes of palladium generally employ soluble palladium(II) chloride or carboxylate complexes with ancillary donors such as amines, nitriles or thioethers. Phosphine donors, for example triphenylphosphine, are frequently used where generation of Pd(0) or low stability Pd(II) complexes are anticipated or required.

In the case of the heterocyclic ligands as donors in cyclometallated systems, for example, pyridine or 2,2'-bipyridyl, the strength of the metal-nitrogen bond is enhanced compared with aliphatic amines due to the π -electron systems associated with the aromatic rings¹⁵ resulting in both σ and π contributions to the bond.

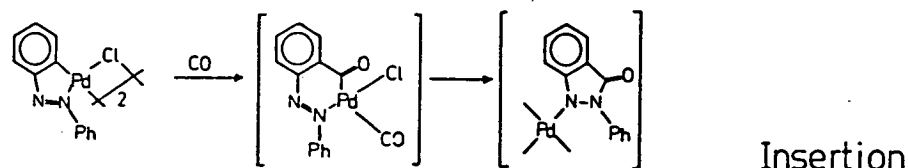
Dialkyl- and alkylhalopalladium(II) complexes containing stabilising phosphine and arsine donors are well known, for example, $[(Et)_3D]PdMe_2$ (where $D = P, As$) and $[(Et_3P)_2PdMeBr]$,¹⁶ but those supported by weaker donor atoms, such as nitrogen, are few.

For unidentate N-donors no such species have been isolated, although $[(bpy)PdMe_2]$ has been reported,¹⁶ and $[(pz_2CH_2)PdMe_2]$ (where $pz_2CH_2 = \text{bis(pyrazol-1-yl)methane}$) and related complexes have been recently isolated and characterised and are stable under ambient conditions.¹⁷ The lack of alkylpalladium complexes with donors other than heavy group VB donors may be largely the result of anticipated instability of the complexes rather than the result of preparative failure.

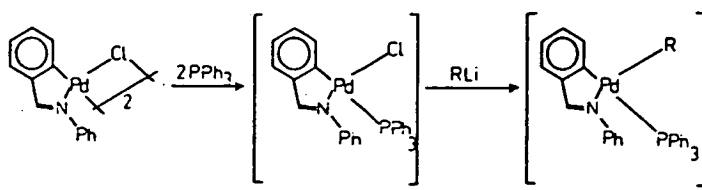
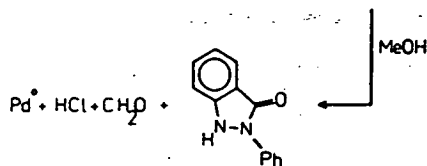
Initial reports of the first cyclometallated compounds involved palladation of azobenzene giving stable monomeric¹⁸ and dimeric products,^{19,20} for example,



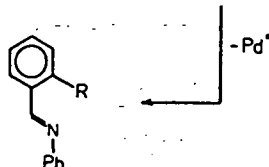
Metal-carbon bonds of this type are susceptible to insertion of unsaturated molecules²¹ and alkylation via Grignard or organolithium reagents.²²



Insertion

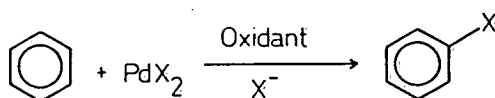


Alkylation



The features of importance in these stoichiometric reactions are that no direct functionalisation of the ortho position of the aromatic substrate is required, and palladation is usually regiospecific. In the latter case this process provides a convenient method for selective synthesis of some ortho-alkyl substituted aromatic compounds which are otherwise difficult to prepare.

Phenylpalladium(II) species supported by the presence of P-donors are stable.^{23,24} However, in the absence of these donors they are postulated to occur as intermediates in the palladium(II) catalysed substitution of aromatic compounds by a wide variety of nucleophiles in the presence of a suitable oxidant such as lead tetraacetate.²⁵

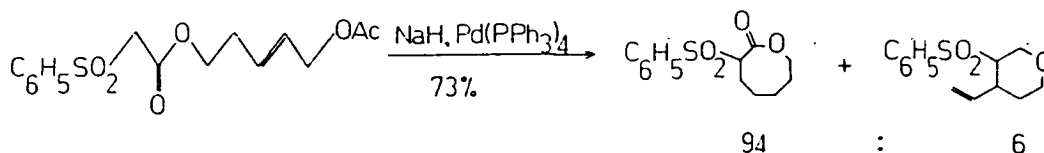


Nucleophiles including acetate, azide, thiocyanate and chloride may be used to form C-O, C-N, C-S and C-Cl bonds. The role of the oxidant is unclear but may be required for the decomposition of the arylpalladium intermediate. Alternatively, the oxidant may oxidise Pd(II) to Pd(IV). Palladium(IV) compounds are known to be capable of oxidising arenes to the observed reaction products.²⁵

Catalytic reactions of Pd(0) complexes often proceed via transient Pd(II) species, generated by oxidative addition, and are usually performed in the presence of phosphine donors that stabilise both the Pd(0) complex as well as the active Pd(II) component. For example, in carbonylation reactions performed in the presence of Pd(0), the catalytically active species is formed on addition of HCl to a coordinatively unsaturated palladium(0) triphenylphosphine complex, $[(\text{Ph}_3\text{P})_2\text{Pd}]$, to give $[(\text{Ph}_3\text{P})_2\text{PdHCl}]$.²⁶ In general, the complexes containing Pd-C σ -bonds formed in the catalytic cycle are not isolable although a number of the hydride complexes have been isolated and structurally characterised, for example, *trans*- $[(\text{Et}_3\text{P})_2\text{PdHCl}]$.²⁷

The synthetically important Pd(0) catalyst, $[(\text{Ph}_3\text{P})_4\text{Pd}]$, has found numerous applications including, for example, the cross-coupling of vinyl halides with a variety of Grignard²⁸ and

lithium reagents.²⁹ Catalytic intramolecular cyclisation to give medium-ring lactones has been accomplished regioselectively using this reagent and shows that a kinetically less favoured ring size can be obtained predominantly.



Reactions of this type may proceed via π -allylpalladium species,³⁰ and similarly, π -allylpalladium complexes derived from vinyl lactones have been employed as templates to relay stereochemistry.³¹ Many other applications of π -allylpalladium compounds in synthesis have been reported.³²

Thus, the investigation of palladium(II) complexes of ligands capable of bonding in a variety of modes, including N-chelation (*N,N*), anionic chelation (*N,C*(aryl); *N,C*(alkyl)), and π -allylic bonding, is of importance in the modelling and understanding of the intermediates produced in the stoichiometric and catalytic reactions mentioned.

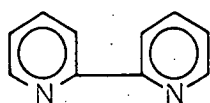
In this study, the research presented describes an investigation of the inorganic and organometallic chemistry of palladium(II) with polydentate pyridine N-donor ligands and their derivatives. These ligands have been chosen since, to date, little work has been undertaken on the coordination of flexible polydentate pyridine ligands with Pd(II), and the number of examples of alkylpalladium(II) complexes stabilised by chelating pyridines is limited.

To achieve the broad objectives (see below) of this study two criteria fundamental to ligand choice and design have been used; the ligands should allow the usual square planar geometry of the metal to be available without severe steric strain, and the ligand synthetic strategy must be suitably versatile to allow prior chemical functionalisation where necessary.

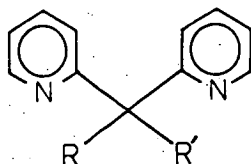
In general, the study of the coordination chemistry of square - planar metals with pyridine and its substituted

derivatives is well represented in the literature. For simple substituted pyridines a large range of ligands have been investigated and are available, frequently from commercial sources. Bi- and tridentate pyridines, including fused pyridines, are also commercially available but the range is more limited. Those most frequently encountered are the bipyridyls, terpyridyls, phenanthrolines, and their substituted derivatives.

Central to this study are the analogues of 2,2'-bipyridyl containing a methylene or methine bridging carbon atom, few of which are commercially available.



2,2'-bpy



bis(pyridin-2-yl)methane
and derivatives

R and R' include
H, Me, Cl, Ph, py.

These have been chosen for the following desirable characteristics,

- i) Bi- and tridentate ligands of this type have N-donor lone-pairs that may all be mutually normal to a coordinated metal atom.^{33,34}
- ii) Bidentate pyridine donors, for example, 2,2'-bpy, are known to stabilise alkylpalladium bonds.^{15,16}
- iii) Ligands of similar structure are known to undergo cyclometallation reactions, for example, 2-benzylpyridine.³⁵
- iv) Their flexibility allows a variety of coordination modes, for example, see pages 30 and 89.

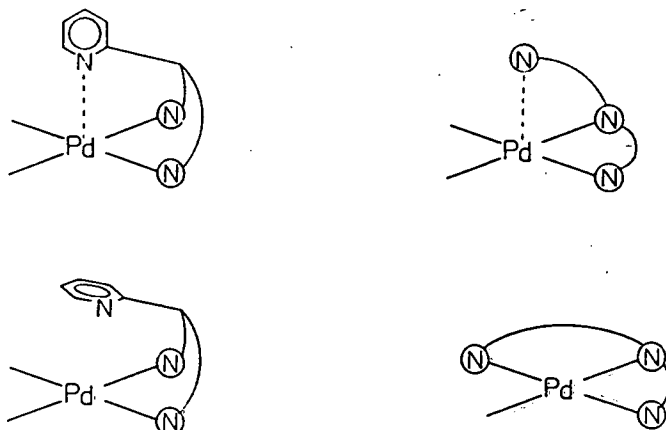
and

- v) The ease of deprotonation of α -methylene and methine alkyl groups allows functionalisation of the bridging group(s) by conventional organic synthetic methods.

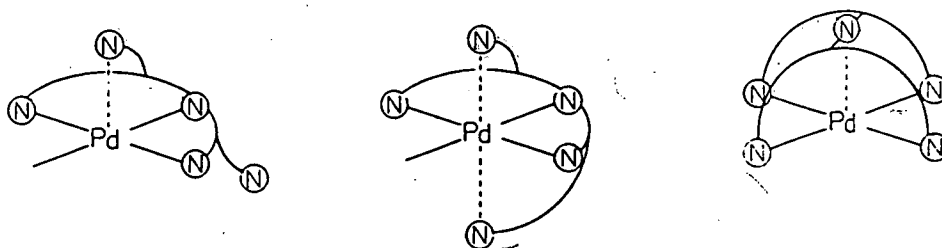
The aims of this work fall into two areas. The coordination properties of inorganic palladium complexes are to be investigated to assess the propensity toward forming higher coordination complexes where this, in conjunction with investigation of some closely related N-donor heterocyclic

ligands and large tri- and pentadentate ligands (where a number of binding modes may occur), will give basic information on normal chelation properties of the ligands with Pd(II). Some possible binding modes of tripodal and related polydentate ligands are shown below.

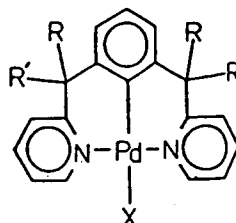
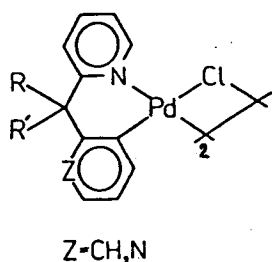
Tridentates



Pentadentate



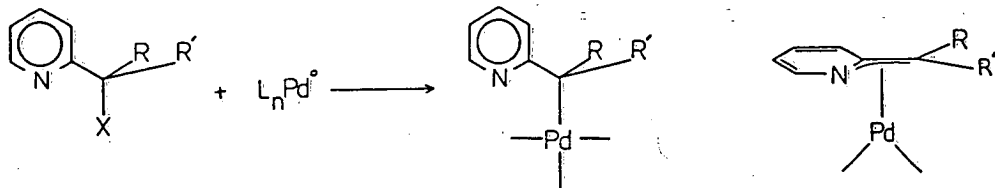
Investigation of organometallic complexes of Pd(II) with these ligands bonding in alkyl, aryl, or allylic modes will be attempted using three methods of forming metal-carbon bonds, (i) Orthometallation, the directed electrophilic attack of palladium on aromatic nuclei, will be assessed with regard to the number and position of donor atoms present required to form complexes of the type shown below.



(ii) Transmetalation, the deprotonation of ligand bridging group by lithium reagents and reaction with derivatives of palladium(II) chloride, will be used to determine whether formation of alkyl or π -allylic palladium bonds is possible.



and (iii), Oxidative Addition, the insertion of Pd(0) into carbon-halogen bonds generating Pd(II) species, will be used to determine conditions necessary for reaction and the effect of the number of ligand N-donors on products isolated.



Where necessary, the factors governing the choice of Pd(II) or Pd(0) substrates will be discussed in the appropriate chapter.

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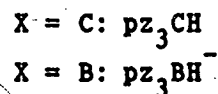
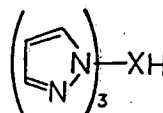
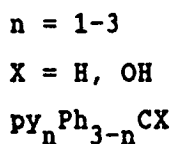
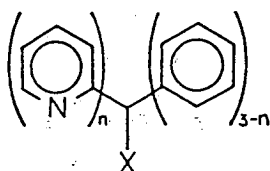
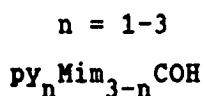
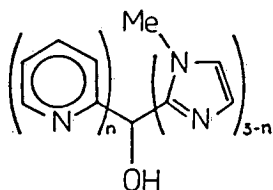
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CHAPTER TWO

INORGANIC COMPLEXES OF PALLADIUM(II) WITH PYRIDINE N-DONOR LIGANDS*

2.1 Introduction

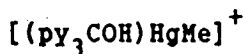
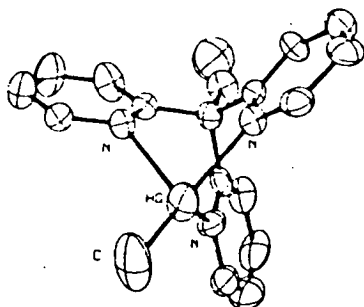
The investigation of coordination properties of N-donor heterocycles, in particular those linked by a bridging carbon atom, has been of continuing interest in this laboratory for the assessment of potential to enlarge the normal coordination environment of the organometallic Lewis acceptors Hg(II)Me , Au(III)Me_2 , Pt(II)Me_2 , and more recently, Pd(II)Me_2 and Pd(II)MeX (where X = halogen). Representatives of the ligands used in these studies are illustrated below.



Using some of these, and related ligands, it has been shown for the cation $[\text{LHgMe}]^+$ that coordination numbers 3 and 4 may be attained in both the solution and solid states.¹⁻⁴ Expansion of the coordination sphere from the usual digonal coordination in, for example, $[(\text{py})\text{HgMe}](\text{NO}_3)$,⁵ has been interpreted in terms of the residual Lewis acidity remaining on the metal center after unidentate N-donor coordination and an appropriate ligand geometry for further, weaker interaction(s).

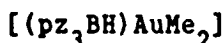
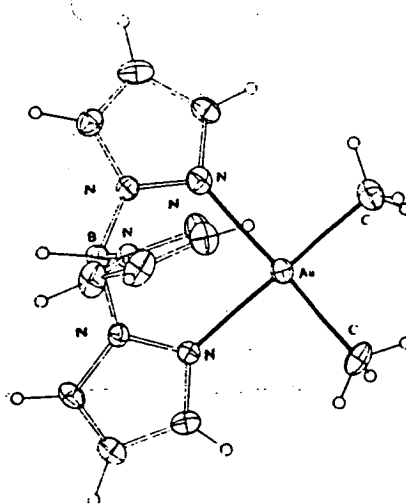
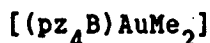
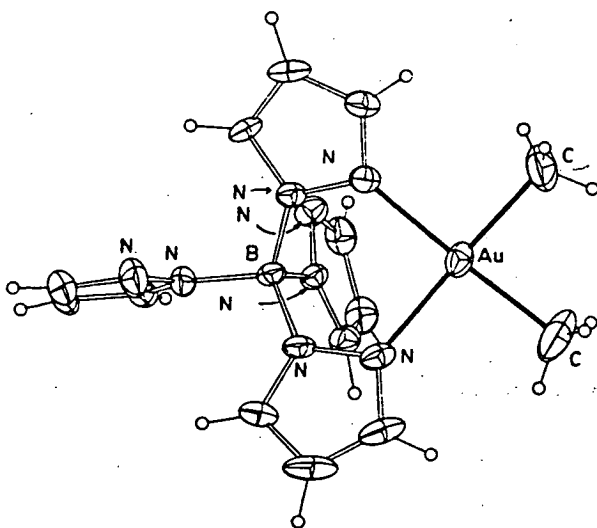
The methylmercury(II) nitrate complex of the ligand py_3COH^2 , below, has Hg-N bond lengths in the range 2.28(1) - 2.53(1) Å and N-Hg-N bond angles in the range 75(0) - 76(0)°.

* For publications concerning this chapter see Publications 4 and 5, pages 228 and 234, respectively.



Thus, the ligand geometry is appropriate for study of axial interactions of square-planar acceptors, for example Au(III)Me_2 , allowing the possibility of square-pyramidal coordination.

Structurally characterised complexes of tripodal N-donor ligands with d^8 dimethylmetal moieties all show the expected domination by square-planar geometry. Dimethylgold(III) nitrate complexes of the potentially tridentate ligands py_3CH (ref. 6), pz_3CH (ref. 6), pz_3BH^- (ref. 7), and pz_4B^- (ref. 8) (where py = pyridin-2-yl and pz = pyrazol-1-yl) contain a square-planar $\text{cis-C}_2\text{AuN}_2$ kernel in the solid state with ligands present as bidentates with one or more uncoordinated donors. For these complexes in solution ^1H nmr studies indicate rapid exchange between coordinated and uncoordinated donors with exchange presumed to involve a 5-coordinate transition state.



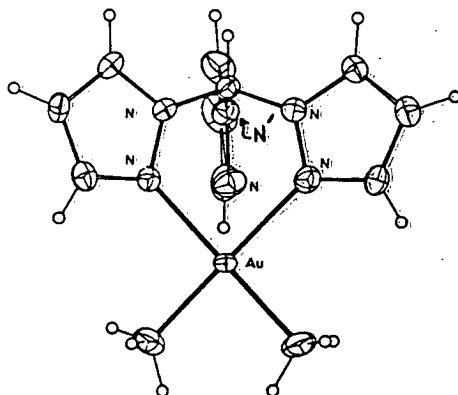
For the complex $[(\text{pz}_4\text{B})\text{AuMe}_2]$ a number of exchange processes are indicated. Spectra at -90°C show three pyrazole environments, two coordinated, one axial*, and one equatorial*. From ca. -60°

* Considering the six-membered chelate ring as an analogue of cyclohexane in the boat conformation. This method of denoting positions of uncoordinated groups will be used hereafter.

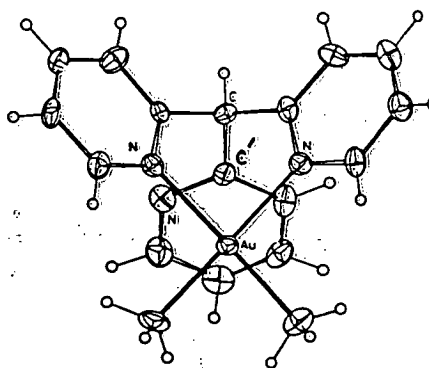
to -15° rapid inversion of the chelate ring occurs making uncoordinated pyrazole environments equivalent, allowing only two pyrazole environments to be observed. At higher temperatures further simplification occurs, with line broadening, arising from exchange of uncoordinated for coordinated pyrazole groups, presumably via 5-coordinate intermediates.

Similar spectral interpretations have been reported for $[(pz_3BH)AuMe_2]^7$, $[(pz_3CH)AuMe_2]^+{}^9$, $[(pz_3BH)AuCl_2]^{10}$, and palladium complexes of pz_4B^- (ref. 11), with 5-coordinate intermediates suggested in all cases.

In contrast, for the complex $[(pz_3CH)AuMe_2](NO_3)$, 1H nmr and solid state studies indicate that a weak axial interaction is present.⁶



$[(pz_3CH)AuMe_2]^+$



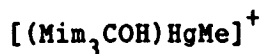
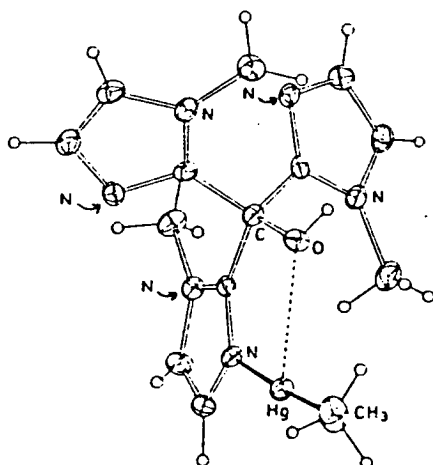
$[(py_3CH)AuMe_2]^+$

It has been proposed that the diminished basicity of pz_3CH compared with related (pyrazol-1-yl)borate and (pyridin-2-yl)methane ligands, and presence of five membered aromatic rings, results in donor strength and a geometry more favourable for a weak axial interaction.⁶ The low Lewis acidity of the C_2AuN_2 kernel is satisfied by the rotation of the axial pyrazole group to give a long $Au...N$ interaction of $3.139(7)\text{\AA}$.

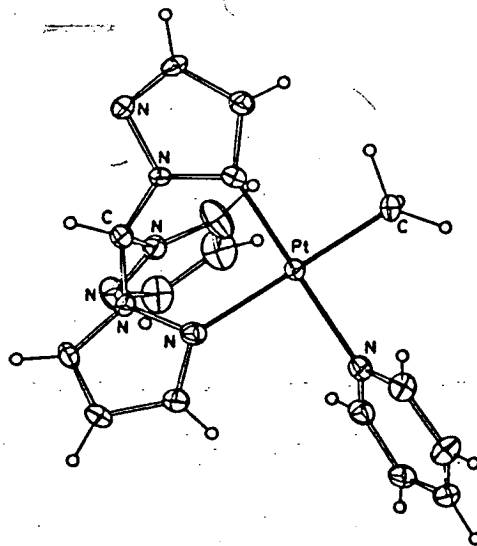
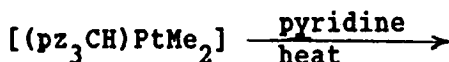
Bidentate py_3CH has an $Au...C'$ distance of $3.064(12)\text{\AA}$, much shorter than $Au...N'$, $3.703(5)\text{\AA}$ in $[(pz_3CH)AuMe_2]^+$. Thus, rotation of the pyridine ring about $C'-CH$ results in an $Au...N$ (axial) distance suitable for a strong bond but inappropriate for the low acidity of $Au(III)$.

Similar observations of the behaviour of $[HgMe]^+$ with strong imidazole donors have been noted. In the complex below, coordination of a second (strong) N-donor is rejected and

residual Lewis acidity of the metal is satisfied by a very weak interaction with an oxygen atom.¹²



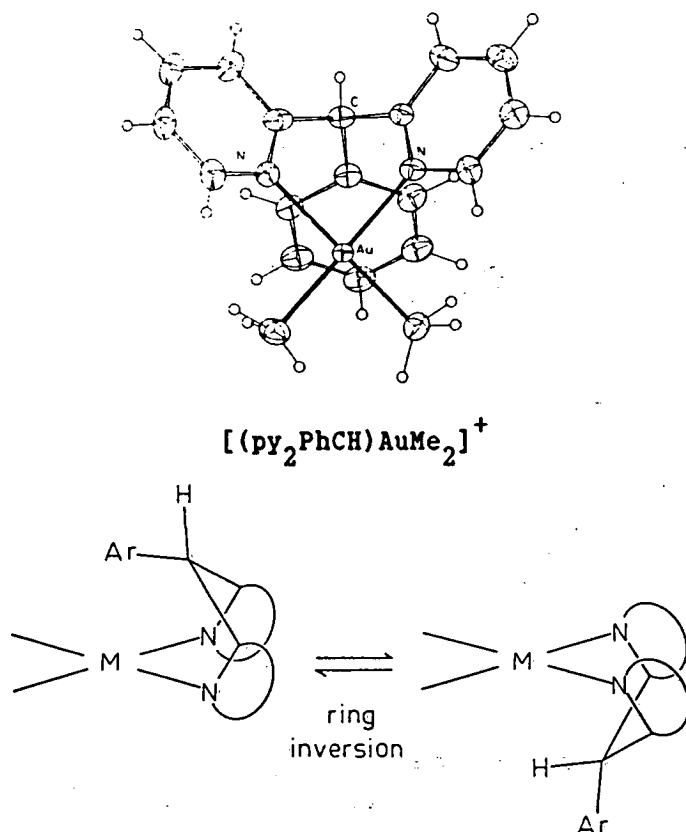
Attempts to study solution and solid state structures of a related platinum(II) complex, $[(\text{pz}_3\text{CH})\text{PtMe}_2]$, have been unsuccessful due to solubility difficulties. However, arising from attempts to find a suitable recrystallisation solvent for this complex metallation products were isolated containing the ligand pz_3CH as a bidentate anion (C,N), and as a nonchelating anion (C).¹³ No axial interactions were evident in these complexes.



As expected for the d^8 metal ions Pd(II), and Au(III), little tendency toward higher coordination geometry has been found.

A frequently observed feature in the solid state structures associated with the coordination complexes of the tripodal and

bidentate-triaryl ligands, for example in $[(py_2PhCH)AuMe_2](NO_3)^6$, is the predominance of structures containing an axial aromatic ring.



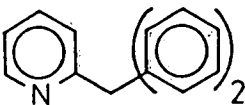
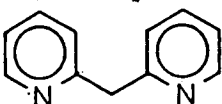
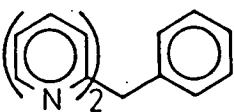
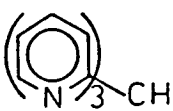
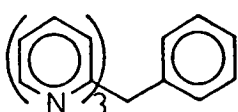
It is clear that for such complexes two conformational arrangements are possible, related by ring inversion, and these have been required to explain, for example, the solution behaviour of the complex $[(pz_4B)AuMe_2]$, previously described.

The ligand configuration in solution is also apparently dominated by axial orientation of aromatic substituents in complexes of triarylmethyl ligands possessing two or more donor groups. Molecular models suggest that the equatorial site of the methylene or methine linkage is more sterically hindered than the axial site. Thus, the substituent of greatest steric demand is positioned over the metal center while substituents of lesser bulk reside between the chelated aromatic groups. Supporting this view is the observation that reported 1H nmr spectra of complexes of those ligands possessing a methine proton show a methine chemical shift similar to that found for the free ligand. In comparison, complexes known to have protons in close proximity to a metal center often show a very dramatic downfield shift in resonance position¹⁴ (also see pages 100 and 126).

Thus, the study of coordination complexes of inorganic palladium(II) complexes with the pyridine containing ligands shown below, and similar to those mentioned, is of importance in determining the interrelationships between Lewis acidity of the metal, donor ability and ligand geometry, and conformational requirements of the organic substrates. The work presented in this chapter attempts to define the major factors governing the coordination environment about Pd(II) in the presence, and under the influence of, ligands that may encourage expansion of the normal coordination sphere.

2.2 Coordination Complexes of Palladium(II) Acetate with Simple Ligands*

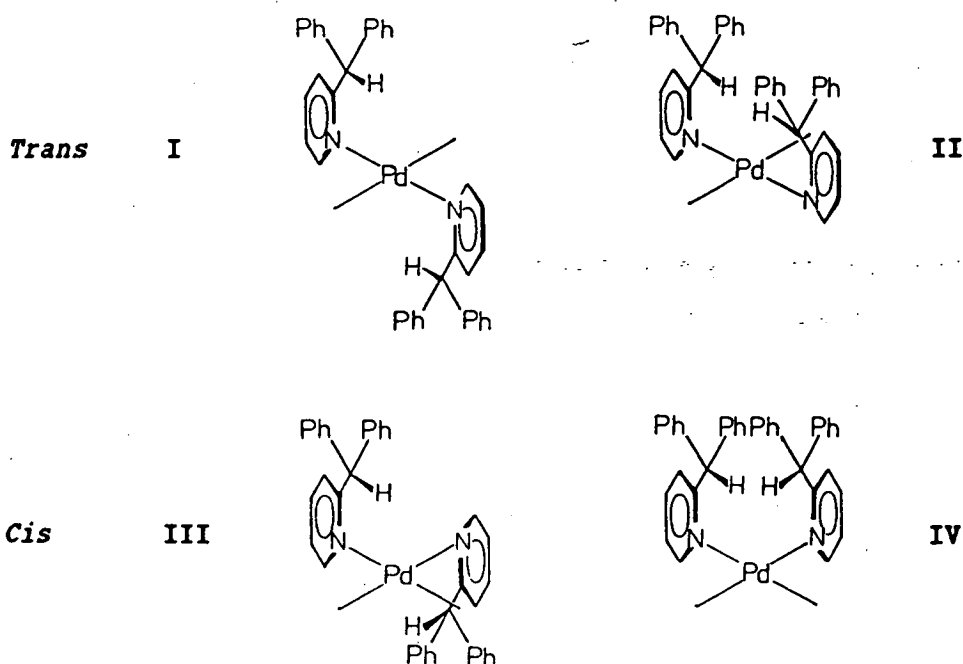
Inorganic complexes of the type $[L_n Pd(OAc)_2]$ have been prepared from ligands containing one bridging carbon atom shown below.*

<u>Donor(s)</u>	<u>Structure</u>	<u>Abbreviation</u>
Monodentate		pyPh ₂ CH
Bidentate		py ₂ CH ₂
		py ₂ PhCH
Tridentate		py ₃ CH
		py ₃ PhC

* Hereafter the terms "simple ligand" and "extended ligand" will be used referring to those ligands containing one and two bridging carbon atoms, respectively.

The complexes are readily prepared in, and crystallised from, organic solutions on mixing stoichiometric quantities of ligand and $\text{Pd}(\text{OAc})_2$. They have high solubility in most organic solvents but on standing in exposed solutions readily absorb moisture from the atmosphere. In the solid state all are indefinitely stable and are less affected by water. Frequently, solvent molecules are occluded on crystallisation of these complexes. The identity of the complexes and solvate molecules is best determined by ^1H nmr spectroscopy in conjunction with infrared spectroscopy for acetato- groups, for example, I.R. spectra often reveal coordination mode(s) of the acetato- groups(s). Selected spectral data for the complexes and free ligands are compiled in Table 2.1, page 23. Microanalysis indicates that all complexes are of stoichiometry $\text{L} : \text{Pd}(\text{OAc})_2$, 1:1, apart from the complex of the monodentate ligand pyPh_2CH , with $\text{L} : \text{Pd}(\text{OAc})_2$, 2:1. The near I.R. shows that some overlap occurs between ligand absorption bands and ν_{as} and ν_{s} for acetato- groups. For those complexes where ν_{as} and ν_{s} absorptions are unambiguous, monodentate acetato- groups are indicated suggesting monomeric formulations.¹⁵ None of the complexes form conducting solutions in acetone.

The complex $[(\text{pyPh}_2\text{CH})_2\text{Pd}(\text{OAc})_2]$ may have either a *cis* or *trans* configuration as well as having $-\text{CHPh}_2$ substituents above or below the plane defined by ' N_2PdO_2 '.



Acetato - groups omitted for clarity

Molecular models of I-IV suggest that rotation around the Pd-N bonds is hindered and that phenyl substituents must be directed away from the metal to occupy the site of least steric demand, as depicted.

Some information on the disposition of the substituents can be gained on comparison of ^1H nmr spectra of the free ligand and complex, and related complexes (see Table 2.1, page 23).

It is apparent from the tabulated values of acetato- methyl resonances that this group is strongly shielded (1.30 ppm) in comparison with the other complexes prepared (1.99-1.80 ppm). Comparison between chemical shifts of methine and pyridine H(6) protons shows that for $[(\text{pyPh}_2\text{CH})_2\text{Pd}(\text{OAc})_2]$ both are substantially deshielded and hence must be remote from the phenyl substituents. Thus, structures (I) or (III) seem most likely.

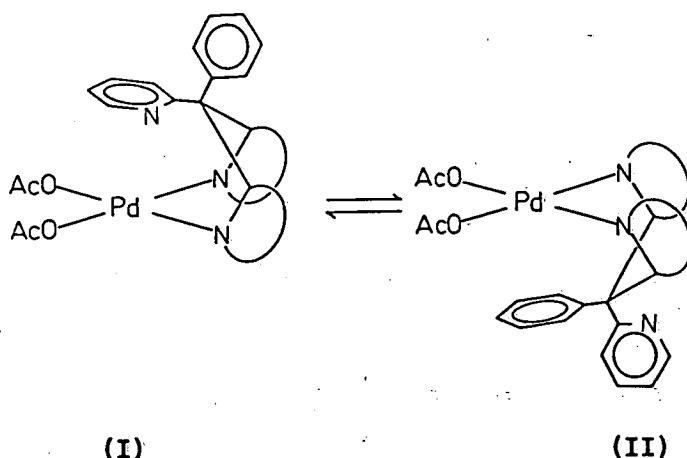
No direct evidence has been obtained to distinguish between the possibilities of *cis* (III), or *trans* (I) isomers. However, comparison with the analogous chloro- complex gives some indication. The complex $[(\text{pyPh}_2\text{CH})_2\text{PdCl}_2]$ (see page 24) exhibits a single Pd-Cl stretching mode at 337 cm^{-1} and a single Pd-N stretching mode at 497 cm^{-1} and is thus clearly of *trans* configuration. As both have very similar ^1H nmr spectra, in particular those regions containing methine and pyridine H(6) resonances, a *trans* configuration for $[(\text{pyPh}_2\text{CH})_2\text{Pd}(\text{OAc})_2]$, (I), is supported.

The ligands py_2CH_2 , py_2PhCH , py_3CH , and py_3PhC clearly form complexes of *cis* stereochemistry with potential for tridentate coordination in complexes of py_3CH and py_3PhC .

At ambient temperature the ^1H nmr spectrum of the complex $[(\text{py}_3\text{CH})\text{Pd}(\text{OAc})_2]$ exhibits features including a broadened pyridine H(6) resonance (8.65 ppm), a methine proton resonance (6.40 ppm), and a sharp methyl (acetato-) resonance (1.91 ppm). On lowering of temperature the H(6) resonance broadens further then resolves at -60°C into signals at 9.04 and 8.64 ppm in 2:1 ratio, respectively. The methine and acetato- resonances both shift, to 5.96 and 2.00 ppm, respectively, but remain sharp. These observations are consistent with rapid exchange of coordinated and uncoordinated pyridine rings presumably occurring via axial association and in-plane dissociation in a "tumbling" motion.

The ^1H nmr spectrum of $[(\text{py}_3\text{PhC})\text{Pd}(\text{OAc})_2]$ exhibits similar features at ambient temperature to the -60° spectrum of $[(\text{py}_3\text{CH})\text{Pd}(\text{OAc})_2]$. Two resolved pyridine H(6) resonances are observed at 9.05 and 8.65 ppm in 2:1 ratio, respectively. On warming to 50°C the features broaden but coalescence is not observed.

In this instance the factors reducing the rate or inhibiting the exchange process, compared with that for the complex of py_3CH , must be related to the arrangement of substituents on the bridging carbon atom.



Chelate Ring Inversion

As a conformation similar to (I) would be required for intramolecular donor exchange, ring inversion may be necessary, and a suitable angular arrangement of the axial N-donor may also be necessary but discouraged by steric demand of the phenyl substituent.

The exchange process for $[(\text{py}_3\text{CH})\text{Pd}(\text{OAc})_2]$ may be more rapid owing to minimal steric demand of the methine hydrogen compared with the phenyl group in $[(\text{py}_3\text{PhC})\text{Pd}(\text{OAc})_2]$.

It may be concluded that in these complexes palladium adopts the expected square-planar geometry. After bidentate coordination in the complexes $[(\text{py}_2\text{PhCH})\text{Pd}(\text{OAc})_2]$ and $[(\text{py}_3\text{CH})\text{Pd}(\text{OAc})_2]$ the remaining aromatic group is in an axial position, while the methine hydrogen atom is in the more sterically encumbered equatorial position.

Donor group exchange in the complexes $[(\text{py}_3\text{CH})\text{Pd}(\text{OAc})_2]$ and $[(\text{py}_3\text{PhC})\text{Pd}(\text{OAc})_2]$ is more rapid in the former and is presumed

to occur via 5-coordinate intermediates. Exchange in the latter is apparently limited by restricted rotation of the axial pyridine ring and chelate ring inversion. The third donor is unlikely to be coordinated, although weak interaction cannot be excluded.

Selected Spectral Data for $[L_n Pd(OAc)_2]$ Complexes and Free Ligands.

Ligand, L(n)	1H nmr ¹					I.R. ²		
	Pyridine H(6)		Methylene or Methine		Acetate	Acetate		
	Ligand	Complex	Ligand	Complex	Complex	ν_{as}	ν_s	$\Delta\text{ cm}^{-1}$
pyPh ₂ CH (2)	8.50	9.48(br)	5.52	7.78	1.30	1594	1374/1360	220/234
py ₂ CH ₂ (1)	8.53	8.63	4.37	5.07	1.99	1566	1394	172
py ₂ PhCH (1)	8.45	8.24	5.69	6.24	1.82	1630	1376/1360	254/270
py ₃ CH (1)	8.52	8.65(br)	5.92	6.40	1.91	1594	1386/1334	208/260
py ₃ PhC (1)	8.47	8.65(1H) 9.05(2H)	-	-	1.80	1634	1362/1308	272/326

1. Recorded at 100 MHz in CDCl₃. Shift (δ) in ppm from internal T.M.S.

2. Two values for ν_s are recorded where ambiguity exists between ligand and acetate absorption bands.

N.B. Full details of 1H nmr spectra and other spectral and physical properties are recorded after preparative details in the Experimental Section.

Table 2.1

2.3 Coordination Complexes of Palladium(II) Chloride with Simple Ligands.

In general, complexes of the type $[L_nPdCl_2]$ have been prepared by reaction of the ligands (illustrated on page 18) with the benzonitrile complex, $[(PhCN)_2PdCl_2]$, in organic solvents (Experimental, page 181).

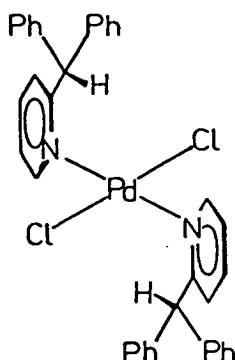
Similar to the analogous acetato- complexes, the chloro-complexes frequently occlude solvent molecules on crystallisation. Most are obtained as sparingly soluble microcrystalline orange solids with the exception of $[(pyPh_2CH)_2PdCl_2]$, which possesses sufficient solubility for 1H nmr spectroscopy, and $[(py_3CH)PdCl_2]$ which was obtained in a highly crystalline form. Thus, in most instances, characterisation has been limited to microanalysis (C,H,N,Cl) and infrared spectroscopy. High resolution mass spectroscopy has been used to detect solvent molecules. The complex of py_2CH_2 was not prepared as this has been previously reported¹⁶, while the complex of tris(pyrazol-1-yl)methane (pz_3CH) has been included for other purposes (see page 46).

The complexes of simple bi- and tridentate ligands have analytical values consistent with a $L:PdCl_2$ ratio of 1:1, and show no conductivity in water or acetone, determined as saturated solutions due to their poor solubility. The complexes are clearly of *cis* configuration, and salt formation, for example $[L_2Pd][PdCl_4]$, which would also account for analysis, may be excluded. The complex $[(pyPh_2CH)_2PdCl_2]$ shows no conductivity in the solvents above and may form *cis* and/or *trans* isomers.

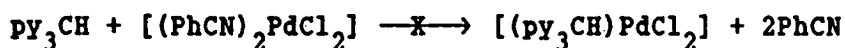
For the related monodentate amine complex $[(NH_3)_2PdCl_2]$ three distinct compounds are known, *trans*- $[(NH_3)_2PdCl_2]$, *cis*- $[(NH_3)_2PdCl_2]$, and the salt, $[(NH_4)_4Pd][PdCl_4]$. The *cis* and *trans* isomers are distinguishable by examination of Pd-Cl and Pd-N stretching modes.¹⁷ For the *trans* isomer one Pd-Cl and one Pd-N stretching mode is observed at 333 and 496 cm^{-1} , respectively. The *cis* isomer displays two Pd-Cl and Pd-N stretching modes at 327 and 306 cm^{-1} , and 495 and 476 cm^{-1} , respectively.

As the complex $[(pyPh_2CH)_2PdCl_2]$ has only one strong absorption in the Pd-Cl stretching region, at 337 cm^{-1} , and in

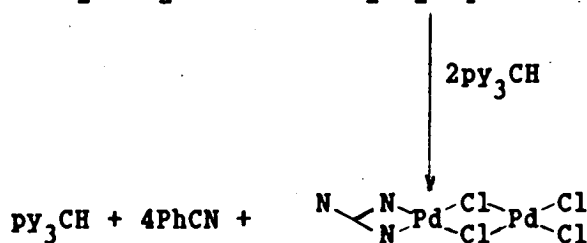
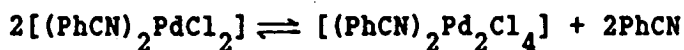
the Pd-N stretching region, at 497 cm^{-1} , it must be assigned a *trans* configuration. No evidence for change in either the ^1H nmr nor I.R. spectra is evident on storage of this complex over a prolonged period (2 years), excluding the possibility of slow *cis* to *trans* isomerism (which has been noted for *cis*- $[(\text{NH}_3)_2\text{PdCl}_2]$ isomerising to *trans*- $[(\text{NH}_3)_2\text{PdCl}_2]$ within 40h¹⁷). From I.R. and ^1H nmr spectral evidence, the structure below is most probable.



Attempted preparation of $[(\text{py}_3\text{CH})\text{PdCl}_2]$ via reaction with $[(\text{PhCN})_2\text{PdCl}_2]$ proved to be unsuccessful.

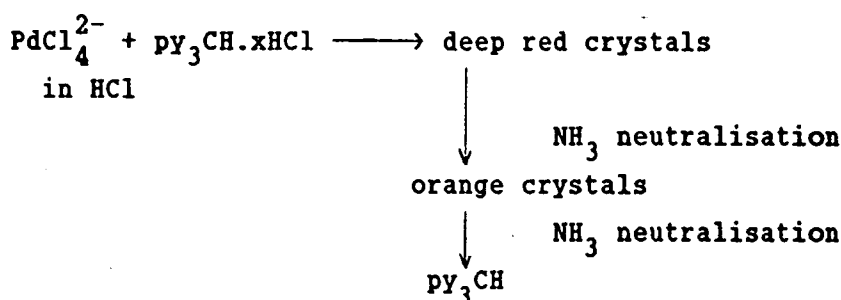


Microanalysis of the very insoluble orange product, obtained from a number of reactions, suggested a $\text{L}:\text{PdCl}_2$ of ca. 1:2, possibly as a result of reaction of the ligand with equilibrium species formed upon dissolution of $[(\text{PhCN})_2\text{PdCl}_2]$ in the solvent (benzene)¹⁸, for example,



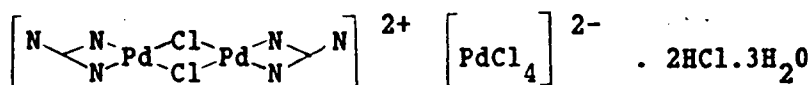
Analysis, Found (%), C 32.4, H 2.1, N 6.6, Cl 26.2
Calc. (%), C 31.9, H 2.2, N 7.0, Cl 23.6.

Subsequently, the preparation was attempted in dilute hydrochloric acid. Dissolution of PdCl_2 and py_3CH in the acid, forming PdCl_4^{2-} and protonating the ligand, and mixing the solutions resulted in an almost immediate precipitation of deep red crystals. On removal of this solid, slow neutralisation of the orange filtrate by enclosure in a sealed chamber with aqueous ammonia solution afforded a crop of bright orange crystals with discharge of solution colour. Continued neutralisation after removal of this solid afforded free ligand, py_3CH , identified by comparison with a pure sample (I.R., M.Pt. comparison).



The orange crystals analysed correctly for the desired product, $[(\text{py}_3\text{CH})\text{PdCl}_2]$, and displayed an infrared spectrum ($4000\text{--}200\text{ cm}^{-1}$) similar to the other bidentate complexes prepared.

Near infrared spectra of the red product showed the probable presence of water and/or a hydrochloride salt as well as absorptions associated with the ligand. Far infrared spectra as a (Nujol mull between polyethylene discs) showed bands at 348 and 325 cm^{-1} (strong), tentatively assigned as Pd-Cl stretching modes. Microanalysis suggested a L:Pd:Cl ratio of ca. 2:3:8 giving rise to a possible formulation " $\text{Pd}_3\text{L}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 3\text{H}_2\text{O}$ ". A number of structural formulations are possible with one shown below, where " 2HCl " may involve the presence of Cl^- and H_3O^+ , or protonation of the ligand.



Analysis Found (%) C 32.9, H 2.6, N 7.4, Cl 24.6

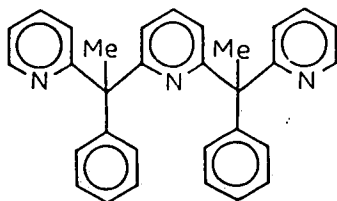
Calc. (%) C 33.3, H 3.0, N 7.3, Cl 24.6.

Dissolution of the product in water (sparing solubility) generates a solution acidic to litmus.

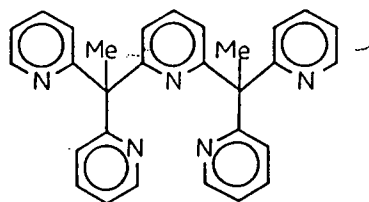
In conclusion, formation of chloro- complexes from $[(\text{PhCN})_2\text{PdCl}_2]$ appears to be a satisfactory procedure for unidentate and bidentate ligands, but is less satisfactory for tridentates. The low solubility of most of the chloro- complexes disallows the use of ^1H nmr spectroscopy as a method for structural elucidation.

2.4 Coordination Complexes of Palladium(II) Acetate with Extended Ligands

To elaborate the investigation of coordination behaviour of inorganic Pd(II) complexes two new extended ligands (containing two bridging carbon atoms), closely related to py_2PhCH and py_3CH , have been prepared.

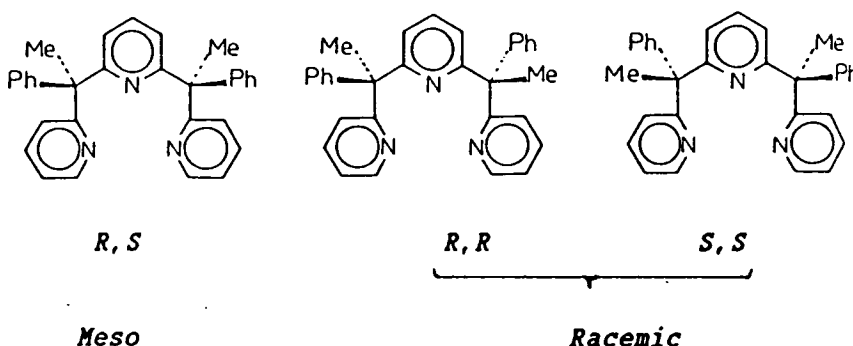


$(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$



$(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}$

The ligand $(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$ clearly contains two chiral centers and is formed as a mixture of *meso* and *racemic* (i.e. *R,R* and *S,S* enantiomers) diastereoisomers.



Molecular models of the *meso* and *racemic* forms of the ligand suggest that both are capable of acting as planar-tridentates toward square-planar metals. With Lewis acceptors such as Hg(II)Me^+ molecular models indicate that both diastereoisomers should be able to act as planar-tridentates (as for $\text{Et}_3\text{tpy}^{19}$) or tripodal-tridentates (as for py_3COH^2).

Using methylmercury nitrate complexes the ligand, composed of mixed diastereoisomers, has been separated into *meso* and *racemic* forms (see Chapter 4, page 90). Thus, *meso*-($\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$, *rac*-($\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$, ($\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$ (unseparated) and ($\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}$ have been individually reacted with Pd(OAc)_2 to give complexes of $\text{L}:\text{Pd(OAc)}_2$ ratio 1:1.

2.4(i) Preparation and Characterisation of the Complexes $[\text{LPd(OAc)}](\text{OAc})$.

Reaction of the extended ligands, above, with palladium acetate by identical methods used for the simple ligands was unsatisfactory, with most attempts yielding gums or products of low crystallinity. To overcome this difficulty (apparently resulting from partial hydration on attempting to isolate the products) water was deliberately introduced into the reaction mixtures via performance of the reactions in open vessels. Thus, both Pd(OAc)_2 and the ligand were dissolved and mixed in small quantities of dichloromethane and allowed to evaporate to dryness in an air draught. Treatment of the resultant orange gums with acetone and ether (see Experimental page 179,180) resulted in isolation of highly crystalline hydrated products.

The products, *meso*- $[(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}]\text{Pd(OAc)}](\text{OAc}) \cdot 3\text{H}_2\text{O}$, *rac*- $[(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}]\text{Pd(OAc)}](\text{OAc}) \cdot 3\text{H}_2\text{O}$, and $[(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}]$

$\text{Pd}(\text{OAc})](\text{OAc}) \cdot \text{H}_2\text{O}$ have all been assigned salt formulation, as all have a conductivity in acetone consistent with 1:1 electrolytes, 42, 52, and $56 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively.²⁰ Reaction of the ligand $(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$ as an unseparated mixture of *meso* and *racemic* diastereoisomers, with $\text{Pd}(\text{OAc})_2$ under these conditions resulted in preferential crystallisation of *meso*- $[(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}]\text{Pd}(\text{OAc})](\text{OAc}) \cdot 3\text{H}_2\text{O}$, in low yield (37%), from acetone. The salts have good solubility in most common organic solvents and limited solubility in water.

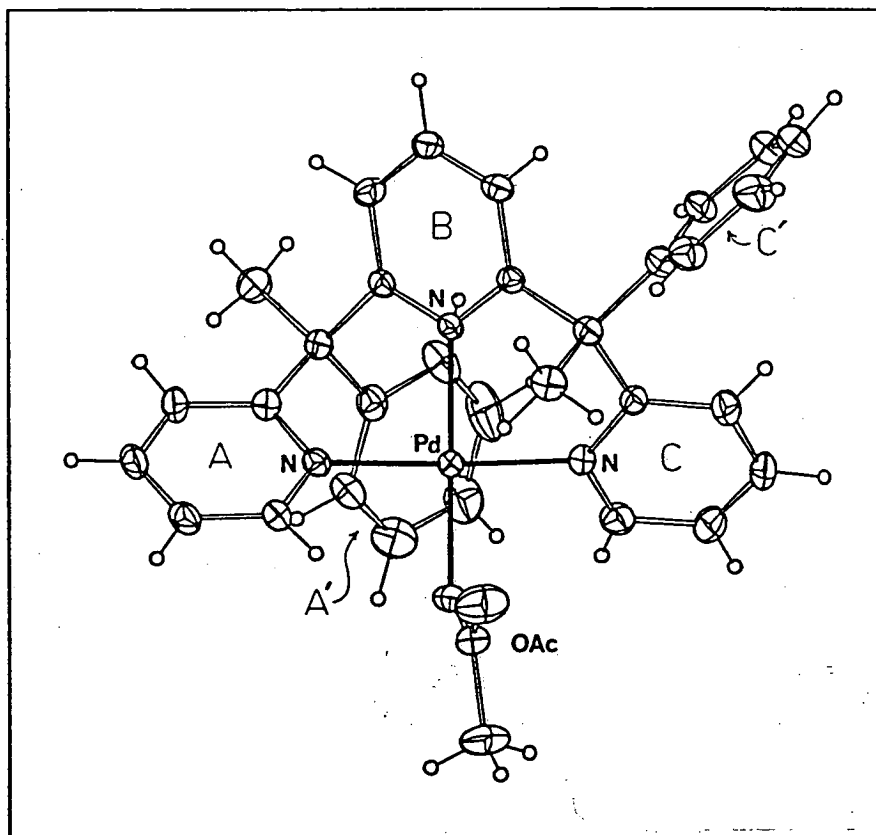
Microanalysis of the complexes of *rac*-($\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$ and $(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}$ suggests trihydrate formulation. However, the *meso* complex, initially isolated as transparent crystals, becomes opaque on drying consistent with partial dehydration. X-Ray analysis of the transparent crystals indicate a trihydrate, while microanalysis of the dried product indicate a monohydrate formulation.

The infrared spectra ($4000\text{--}400 \text{ cm}^{-1}$) of the three complexes show absorptions indicating the presence of ligand, acetate group(s), and water. As for similar acetato- complexes previously mentioned, overlap between ligand and $\nu(\text{CO}_2)$ bands occurs that limits infrared spectroscopy as a method of assigning acetato-group coordination mode(s). For the complexes of *meso*-($\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$ and *rac*-($\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$ the infrared spectra are similar in most regions. However, distinction may be made in the $\nu_s(\text{CO}_2)$ region where the *racemic* complex possesses a sharp strong absorption at 1378 cm^{-1} while the *meso* complex exhibits a weaker broadened absorption centered at 1382 cm^{-1} . For the complex of $(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}$, $\nu_s(\text{CO}_2)$ appears at 1370 cm^{-1} while $\nu_{as}(\text{CO}_2)$ is obscured by ligand absorptions.

From conductivity information, and subsequent X-ray analysis in one instance, tridentate coordination is a minimum requirement for each ligand. For the complex of $(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}$ weak axial interaction is also possible.

2.4(ii) The Solid State Structure of

The title complex is composed of cations *meso*- $[\{(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}\}\text{Pd}(\text{OAc})]^+$, CH_3CO_2^- ions, and water molecules.



Meso- $[\{(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}\}\text{Pd}(\text{OAc})]^+$ from its acetate salt.

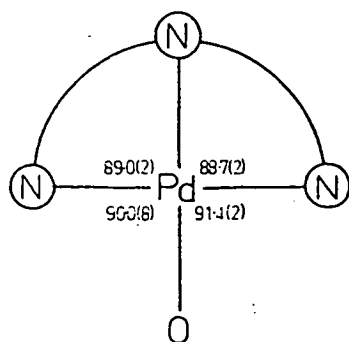
The palladium atom has a square-planar coordination environment with the nitrogen donor ligand present as a planar tridentate. Selected bond lengths and angles for the palladium coordination environment are shown overleaf and full information is included in Publication 4, page 228.

The palladium atom lies close to the projected mean planes of the pyridine rings A and C, 0.067\AA and -0.160\AA , respectively, but is -0.388\AA from the mean plane of the central ring B.

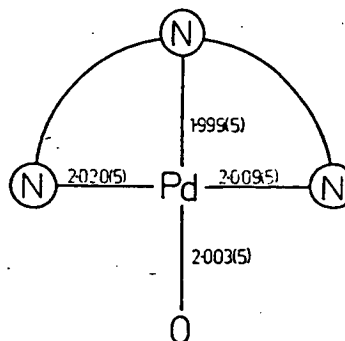
The pyridine and phenyl rings are planar with maximum deviation from the mean planes C_5N or C_6 observed for C(2) of pyridine ring C, 0.028\AA . The coordinated and uncoordinated acetate groups are planar, with maximum deviation from mean planes " C_2O_2 " observed for the carboxylate carbon of the

uncoordinated acetate, -0.14\AA . Neighbouring cations are related by centers of symmetry (space group $P 2_1/c$).

Palladium Environment



Angles (degrees)

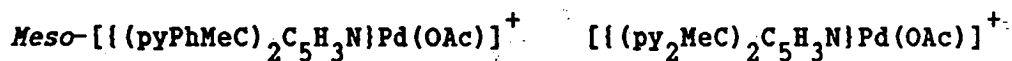
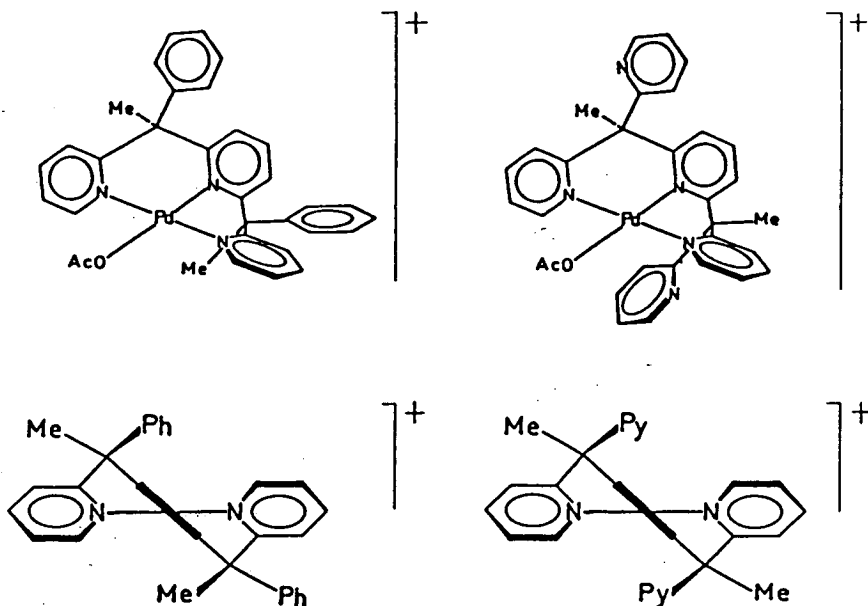


Bond lengths (\AA)

2.4(iii) Solution Structures of the Complexes

From consideration of the solid state structure of *meso*- $[(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}]\text{Pd}(\text{OAc})](\text{OAc}) \cdot 3\text{H}_2\text{O}$, and of molecular models of similar complexes containing the ligands *rac*-($\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$ and $(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}$, the presence of a number of conformers, possibly in equilibrium in the solution state, must be considered for each case. Thus, in conjunction with ^1H nmr spectral results for each complex, possible conformers and their expected ^1H nmr spectral characteristics will be discussed where necessary.

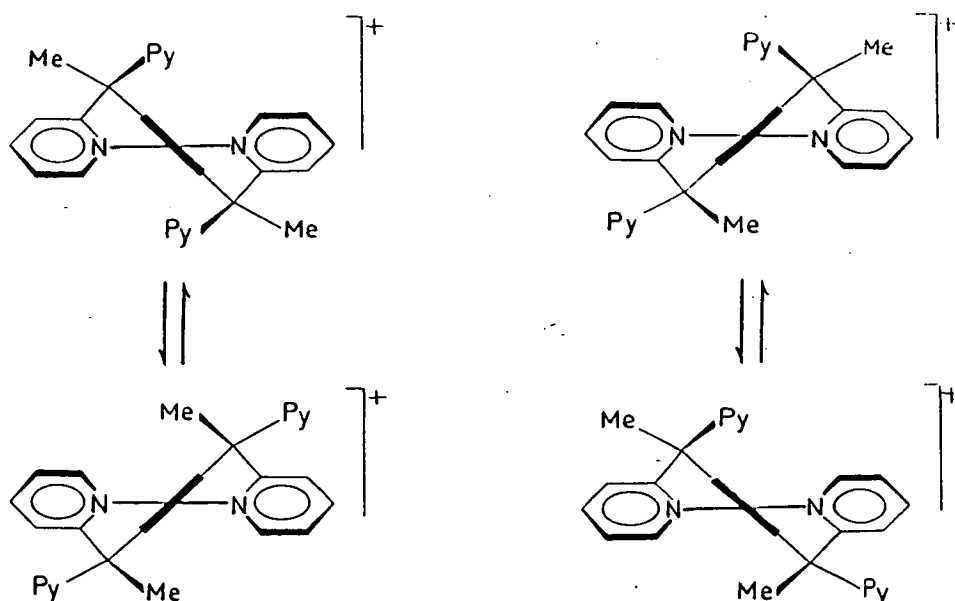
Typical three dimensional representations of the cations *meso*- $[(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}]\text{Pd}(\text{OAc})]^+$ and $[(\text{py}_2\text{MeC})\text{C}_5\text{H}_3\text{N}]\text{Pd}(\text{OAc})]^+$, with diagrammatic representation beneath, are shown below.



In the standard ^1H nmr spectra the most readily identified proton environments are those associated with the pyridine H(6), methyl, and acetato-(methyl) protons, although distinction between bound and ionic acetato- groups, where evident, has not been attempted. Using these characteristic resonances the ratio $\text{L}:\text{Pd}(\text{OAc})_2$ may be deduced, as well as some information on ligand conformation from the number of resonances and chemical shift of, in particular, the pyridine H(6) and methyl protons.



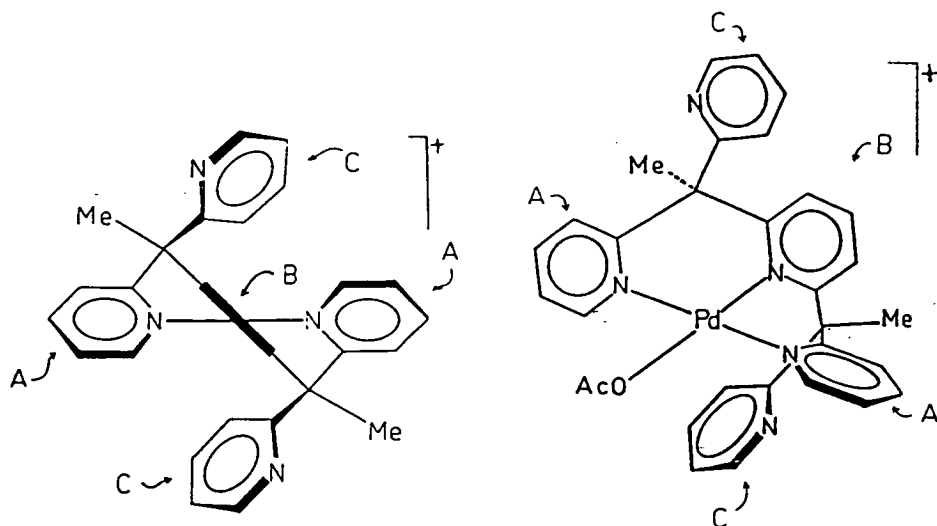
Although the ligand in the title cation contains no chiral centers two distinct forms of planar-tridentate coordination are possible, and conformational effects may be exhibited.



The ^1H nmr spectrum of the title complex as its acetate salt recorded in CDCl_3 at ambient temperature is shown on page 35 with an expansion of the aromatic region on page 36.

Proton environments most readily identified are those occurring at 2.01 ppm, coincident acetato-(methyl) resonances; 2.40 ppm, coincident methyl resonances; 5.03 ppm, water of solvation; and 7.91 and 8.26 ppm, pyridine H(6) protons in equal ratio (2:2). The acetato- resonance position has been assigned by comparison with the structurally characterised complex, *meso*- $[(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}]\text{Pd}(\text{OAc})](\text{OAc}) \cdot 3\text{H}_2\text{O}$ (see pages 30 and 40), while the pyridine H(6) resonances have been assigned by their characteristic splitting pattern and coupling constants, for example, $J(\text{H}(6,5))$ is usually ca. 5Hz.

Observation of only one methyl environment associated with the coordinated ligand (at 2.40 ppm), of similar chemical shift to that found for the free ligand (at 2.21 ppm), and to that for the methyl group remote from palladium in *meso*- $[(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}]\text{Pd}(\text{OAc})](\text{OAc}) \cdot 3\text{H}_2\text{O}$ (at 2.53 ppm, see page 41) suggests the symmetrical structure below (in two representations).

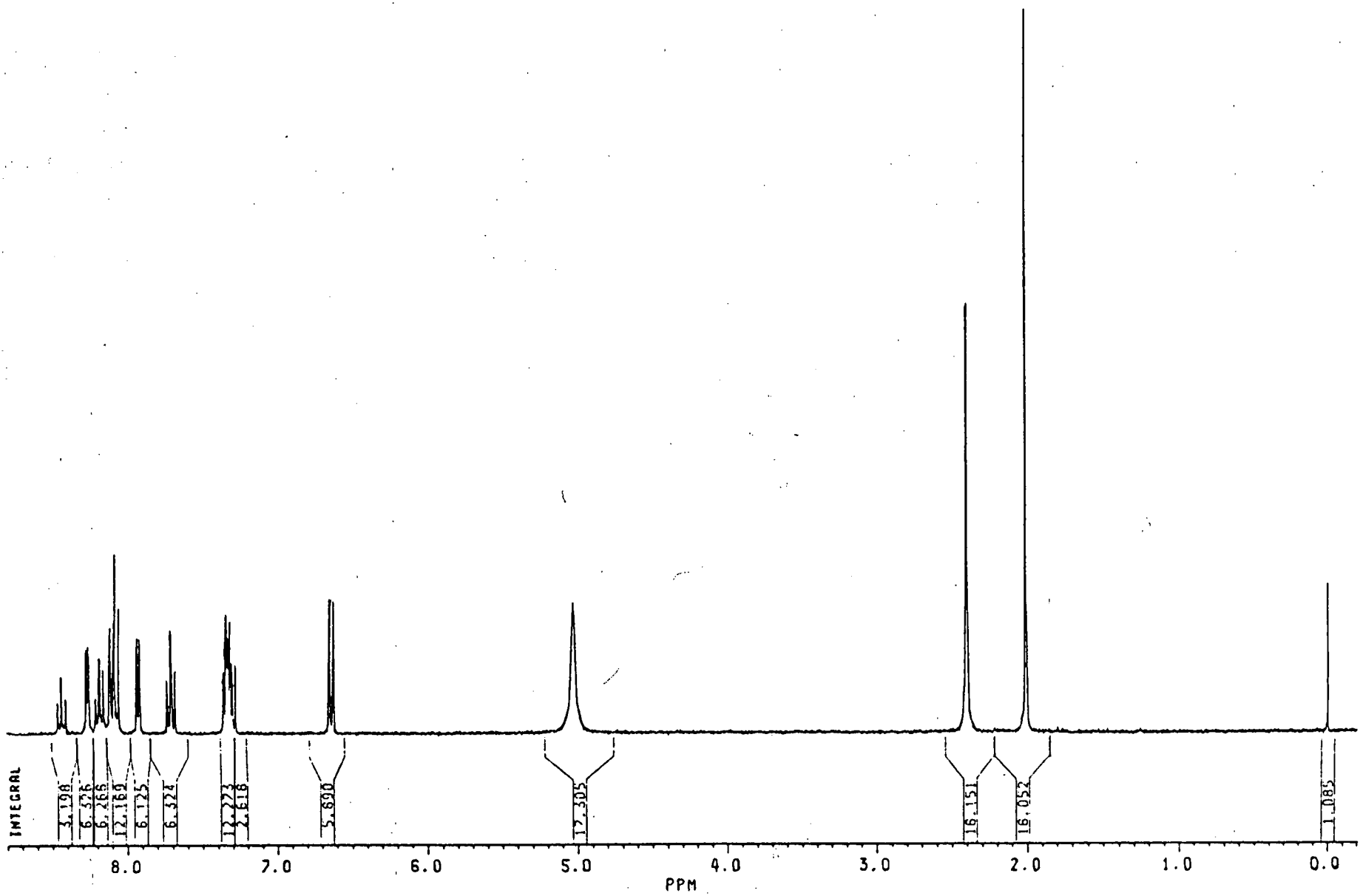


This structure is consistent with the observation of two pyridine H(6) resonances in equal ratio. However, in contrast to the frequently observed downfield shift observed for H(6) resonances on coordination to an electrophile, the H(6) atoms of the terminal coordinated pyridine groups in this cation have been assigned to the upfield resonance at 7.91 ppm (cf. 8.50 ppm in the free ligand) as molecular models suggest that the protons H_A^6 fall within the shielding cones of the uncoordinated pyridine rings (C). The resonance position of the H_C^6 protons (8.26 ppm) more closely resembles that found for the free ligand (8.50 ppm), being shielded to a lesser extent by the terminal coordinated pyridine rings.

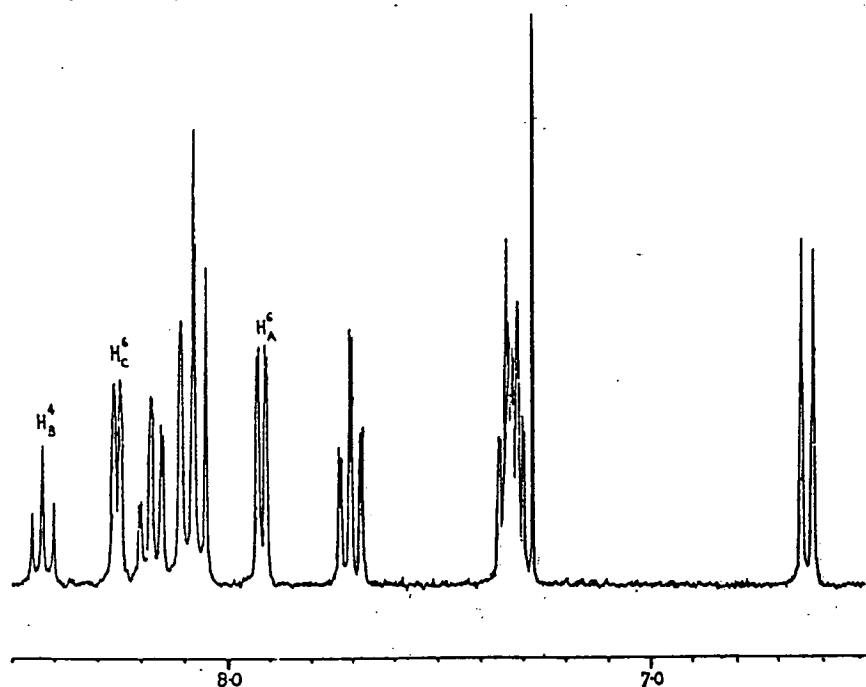
Assignment of other proton resonances within the aromatic region is possible, for example, H_B^4 may be assigned to the triplet observed at 8.43 ppm ($J(H_B^{4,3}) \equiv J(H_B^{5,4}) = 8$ Hz) as it is the only resonance signal that integrates for a single proton. However, without the aid of decoupling experiments further assignments are more tentative, in particular where resonance overlap occurs. Thus, a two dimensional COSY* spectrum has been obtained.²¹⁻²⁴

* Two dimensional homonuclear correlated spectra manifest connectivities between spin-coupled nuclei and provide assignments of individual spin systems in complex 1H nmr spectra.

¹H Nmr spectrum of [l(py₂MeC)₂C₅H₃N]Pd(OAc)₂(OAc)·3H₂O



The COSY spectrum of the aromatic region of the title complex is shown overleaf, and the standard ^1H nmr spectrum of the same region below.

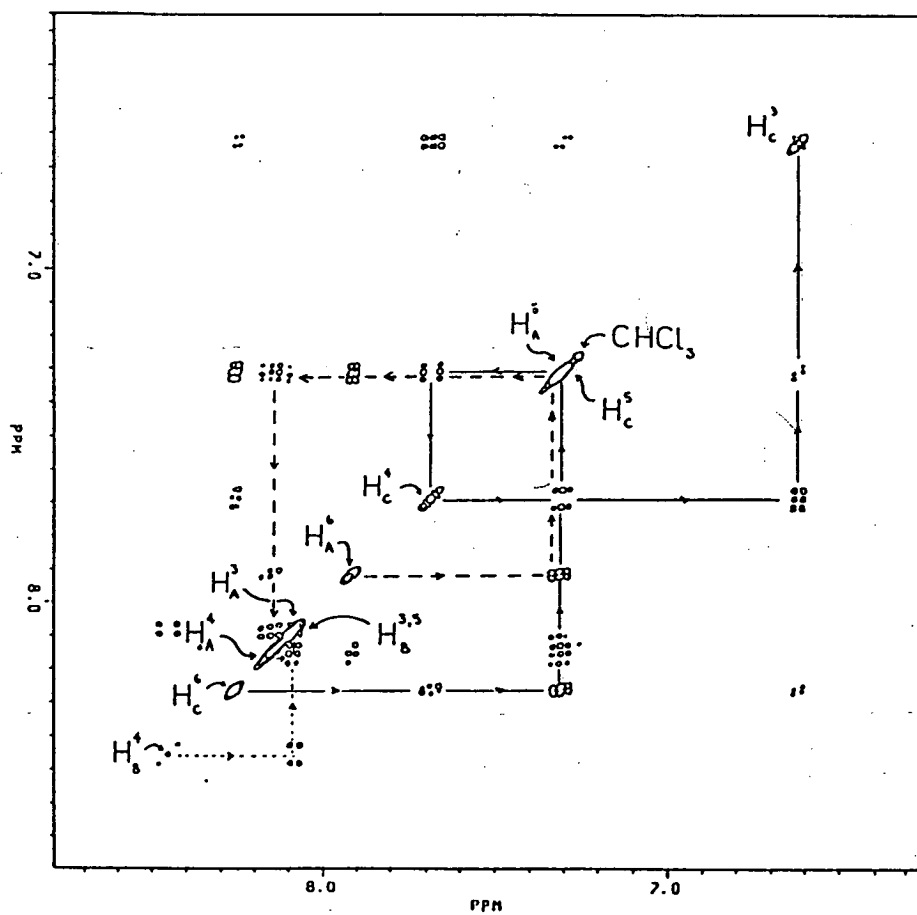
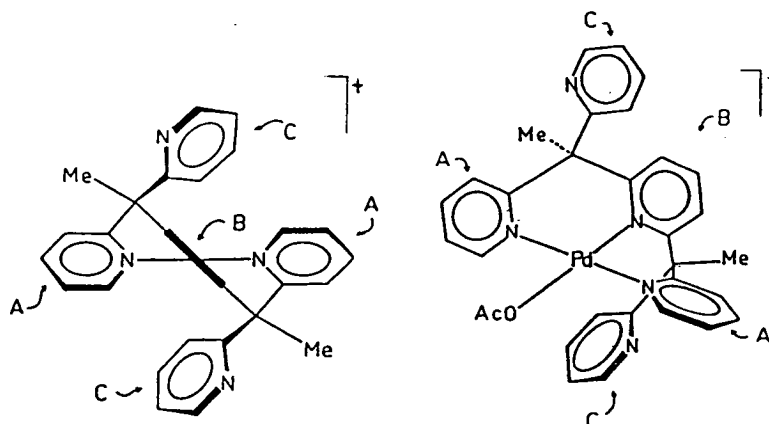


The diagonal from lower left to upper right in the 2D spectrum represents the usual frequency versus intensity spectrum with peak intensity represented by concentric contours. Those contoured regions off the diagonal indicate protons related by proton-proton coupling. For example, the coupling of H_C^3 (upper right) to H_C^4 (middle) is indicated by the lines drawn normal to the frequency axes to the cross peaks. Uncoupled resonances, for example, CHCl_3 , show no cross-peaks.

In the standard spectrum on page 35, one proton environment of each aromatic ring is distinguishable: $\text{H}(4)$ from the central coordinated pyridine ring (H_B^4), and $\text{H}(6)$ from both coordinated and uncoordinated pyridine rings (H_A^6 and H_C^6 , respectively). These resonances are convenient starting points for further assignment of individual ring protons.

COSY Spectrum of $[(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}]\text{Pd}(\text{OAc})](\text{OAc}) \cdot 3\text{H}_2\text{O}$

(Aromatic Region)

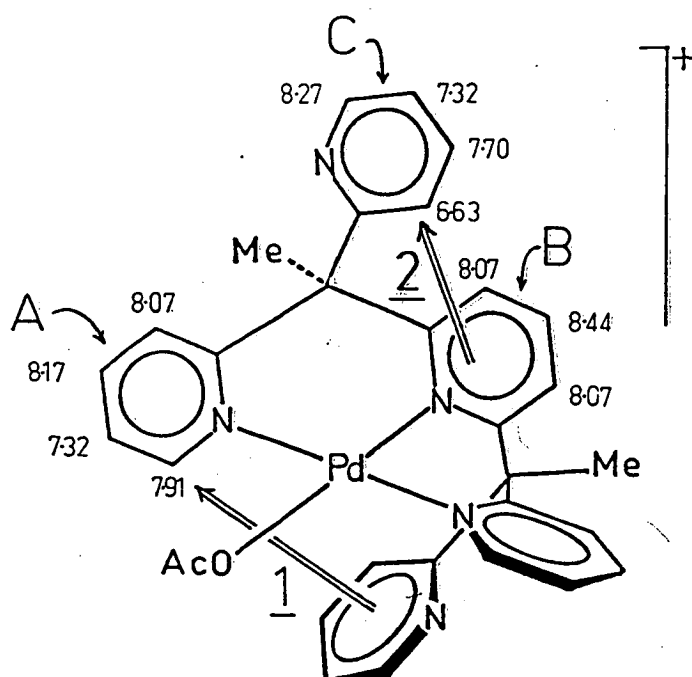


- - - - - Connectivity in Ring A.
 Connectivity in Ring B.
 _____ Connectivity in Ring C.

As the method for assignment of protons in each ring environment is similar, only assignment of protons in the uncoordinated pyridine rings (C) will be given, the others follow by analogy.

The peak designated H_C^6 in the COSY spectrum is coupled to three protons since a line drawn from this peak, normal to the vertical frequency axis, intersects three cross-peaks. The proton H_C^6 is most strongly coupled to H_C^5 resonating at ca. 7.32 ppm.* In turn, H_C^5 is coupled to H_C^4 (7.70 ppm), and H_C^4 to H_C^3 (6.63 ppm).

Following a similar assignment procedure for the remaining rings the following proton shift values may be deduced.



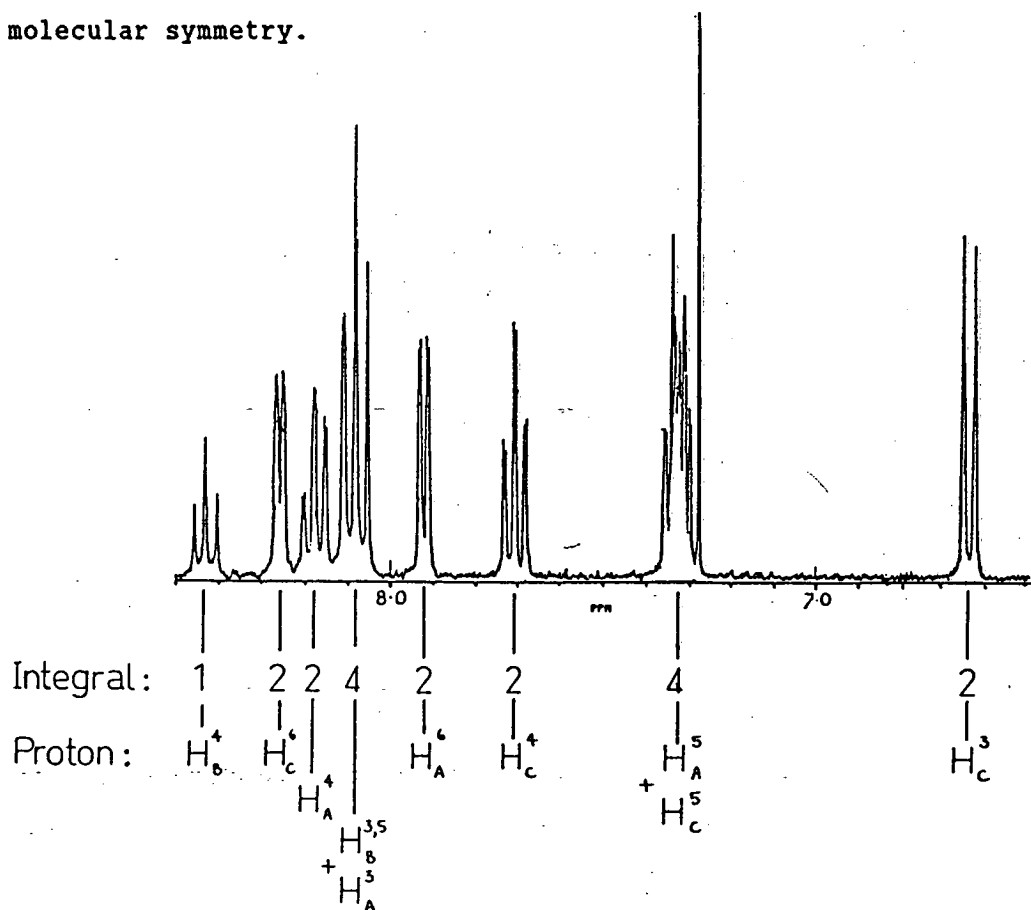
It should be noted that two-fold symmetry about the O-Pd-N_B bond in this cation makes the terminal coordinated and uncoordinated rings respectively equivalent. The shift values recorded here have been read directly from the COSY spectrum and are less accurate than those recorded in the Experimental Section

* The magnitude of the cross peaks indicate proportionally the magnitude of J. However, cross peak intensity may also be influenced by dipole-dipole interaction and nuclear Overhauser effects. The identity of proton environments may be readily checked using other cross peaks arising from the original signal, and by integration ratios after complete assignment.

(page 179) which have been taken from a standard high resolution spectrum.

The shift values are reconcilable with the assertion previously made (page 34) that the terminal coordinated pyridine ring H(6) environments experience shielding from uncoordinated pyridine rings, as shown by arrow 1. The ring orientations are supported by the observation that the protons H_C^3 are strongly shielded by either rings A or C, as shown by arrow 2. The protons H_C^3 resonate at 6.63 ppm compared with H_A^3 and H_B^3 which both appear at ca. 8.07 ppm.

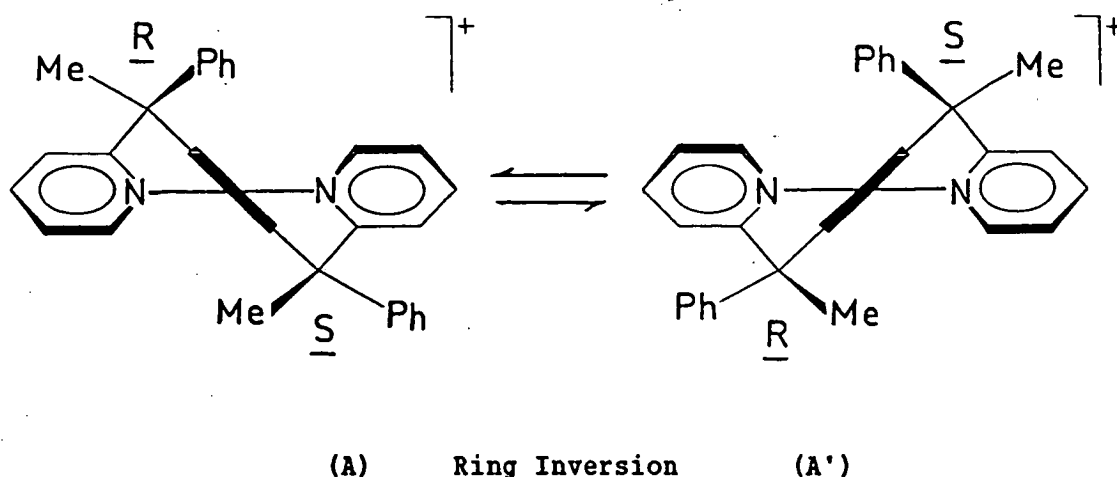
Integration ratios also support the assignments given and these are shown below. It should be also noted that assignments with an A or C subscript represent two protons due to the molecular symmetry.



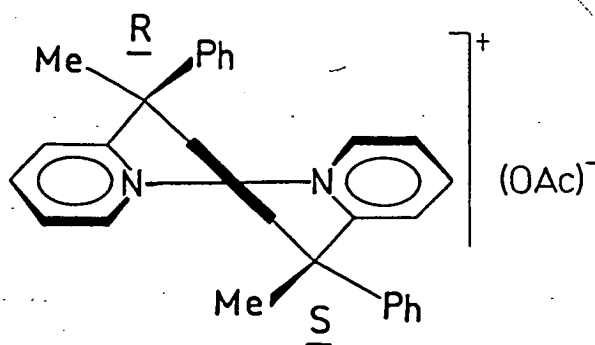
The Cation *Meso*-[(pyPhMeC)₂C₅H₃N]Pd(OAc)]⁺

The schematic representation of the title cation is shown below along with its ring inversion product. From inspection, it is clear that both (A) and (A') would exhibit identical ¹H nmr spectra as (A) and (A') are related by a mirror plane.

For this complex the ligand would be expected to show two chemically distinct pyridine H(6) resonances as well as two distinct methyl group environments. In general, a complex spectrum may be expected for the remaining proton environments as all aromatic rings and substituents reside in chemically inequivalent environments.



The ^1H nmr spectrum of the title complex may be readily interpreted in terms of the structure below, previously discussed on page 30.



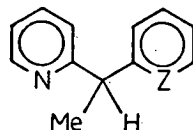
N.B. Coordinated acetate omitted for clarity.

The spectral region containing resonances associated with acetato- and bridgehead methyl groups supports a solution structure similar to that found in the solid state (see page 30). Thus, two chemically distinct methyl group environments are

observed as well as environments attributable to bound and ionic acetate groups, with integration ratio 3:3:3:3. Distinction between bound and ionic acetate has not been made.

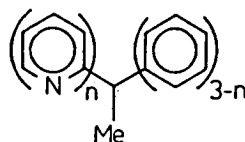
The methyl resonances, Me_A and Me_E , have been so designated (A, axial; E, equatorial) to indicate their relative position with respect to the metal atom and to the six-membered boat conformation chelate rings that support them. The equatorial methyl group has been assigned by its identical chemical shift to the methyl groups in the free ligand at 2.53 ppm, and its similarity in chemical shift to the methylated simple ligands below. The axial methyl group, expected to be shifted downfield due to its proximity to the metal atom (see further comments on page 126), has been assigned to the resonance at 3.30 ppm.

Ligands



Z = CH, 1.65.

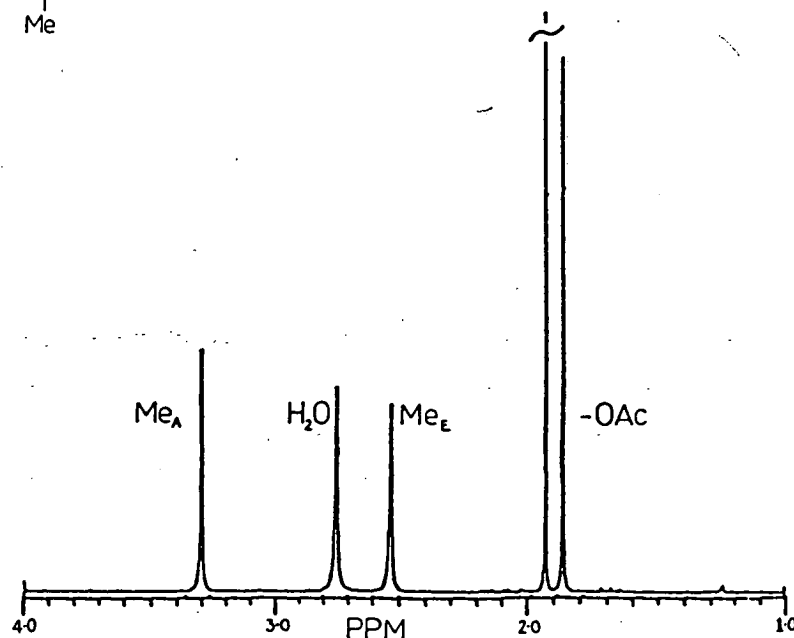
Z = N, 1.74.



n = 1, 2.20.

n = 2, 2.27.

n = 3, 2.27.

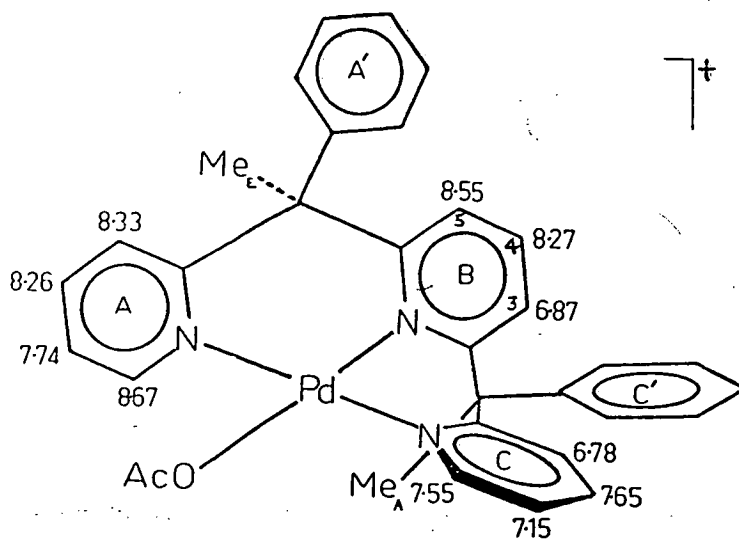


To confirm acetate assignment in the ^1H nmr spectrum the analogous chloro- complex *meso*- $[(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}\{\text{PdCl}\}]\text{Cl}\cdot 2\text{H}_2\text{O}$ was

prepared by metathesis from the acetato- complex, as well as by reaction of the unseparated ligand with $[(\text{Me}_2\text{S})_2\text{PdCl}_2]$ (see Experimental page 183). Infrared and ^1H nmr spectra of the chloro- and acetato- complexes are similar, with absence of acetato- features in the I.R. and ^1H nmr spectra for the former complex. The ^1H nmr spectrum of the chloro- complex shows Me_A at 3.20 ppm and Me_E at 2.63 ppm.

As the cation of the title complex has much lower symmetry compared with that complex containing $(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}$, the number of aromatic resonances in the standard ^1H nmr spectrum is substantially greater, and resonance overlap more common. Thus, for interpretation of the COSY spectrum of the title complex, overleaf, the protons H_A^6 (lower left) and H_B^3 and H_C^3 (upper right) have been used as starting points for ring assignment.

In a similar manner to that previously described, the following assignment of pyridine proton chemical shifts has been made.

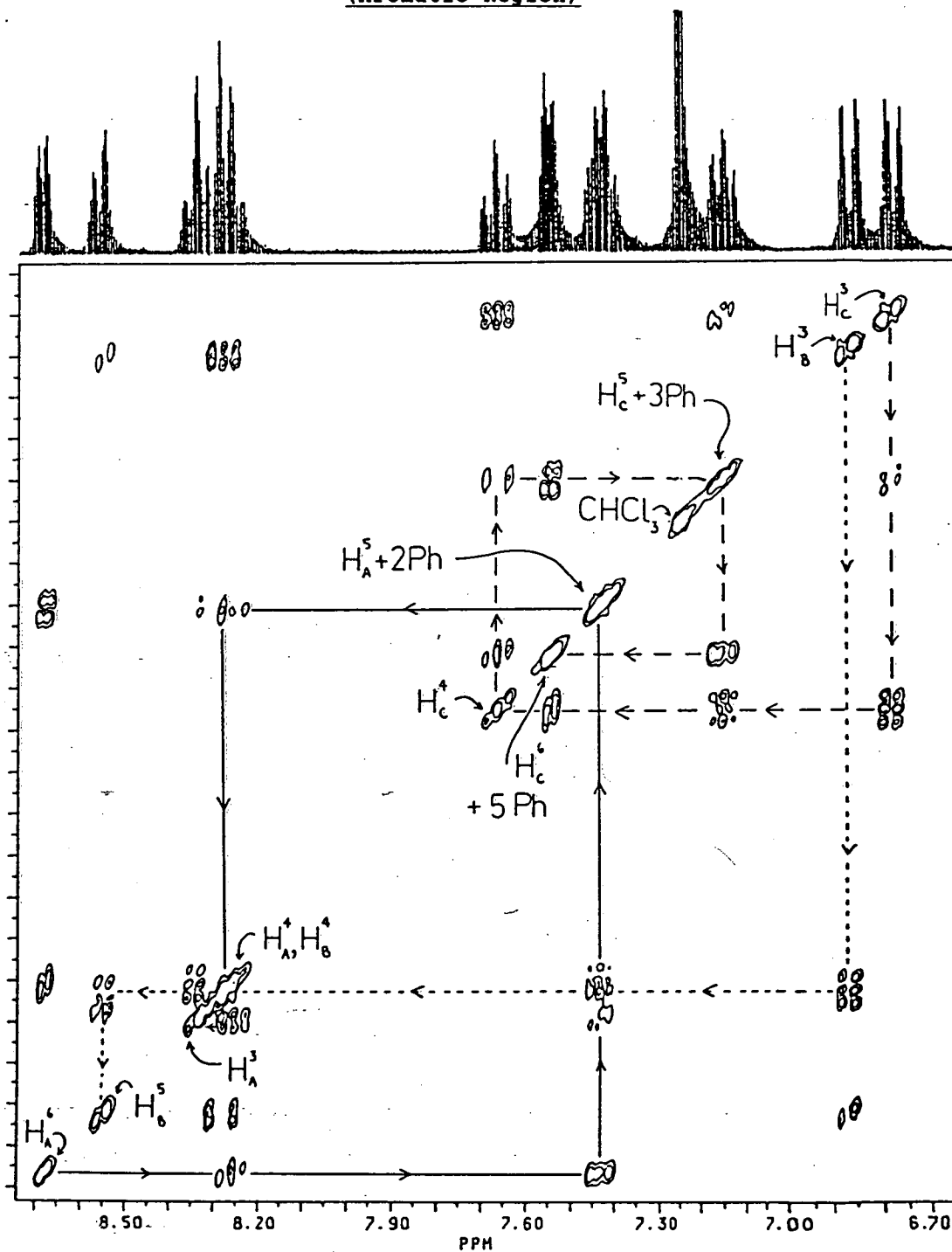


The structure suggested by the standard ^1H nmr spectrum of the region containing methyl and acetato- resonances (page 41) is substantiated by the shift values found for the pyridine donors.

Thus, the proton H_A^6 (8.67 ppm) resonates at a similar chemical shift to that found in the free ligand (8.52 ppm), and is relatively unaffected by other ligand substituents. Proton H_C^6

COSY Spectrum of *Meso*-[$\{(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}\}\text{Pd}(\text{OAc})\}(\text{OAc})\cdot\text{H}_2\text{O}$

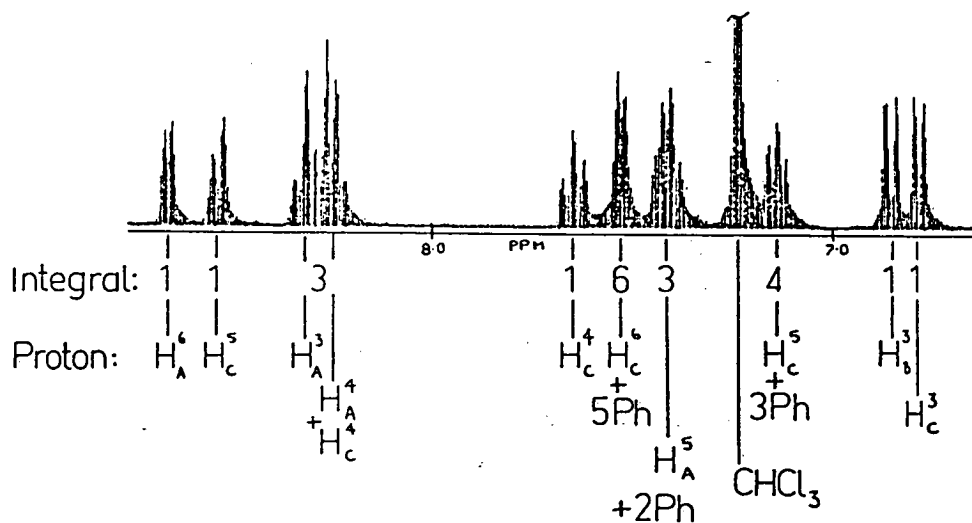
(Aromatic Region)



--- Connectivity in Ring A.
 Connectivity in Ring B.
 ——— Connectivity in Ring C.

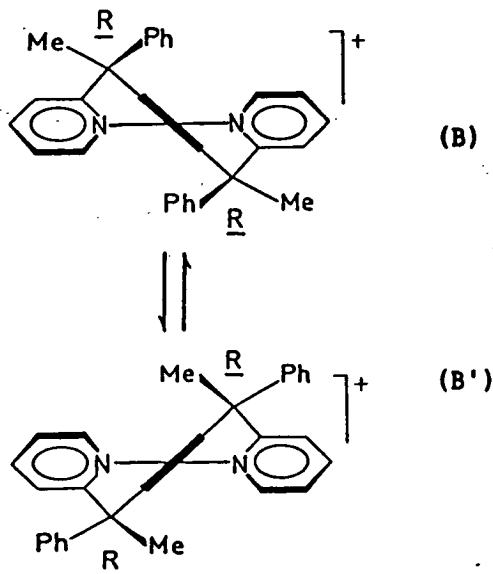
(7.55 ppm) is shifted upfield from the free ligand resonance due to the shielding effect of phenyl ring A'. Those protons within the shielding influence of phenyl ring C' (H_B^3 and H_C^3) exhibit substantial upfield shift in comparison with related protons, for example, H_B^5 and H_A^3 .

Phenyl proton shift positions have been assigned from the integration ratios below, but although phenyl substituents A' and C' are different, assignment of individual protons for these cannot be made with certainty.



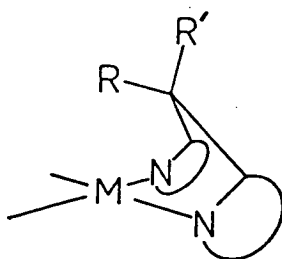
The Cation $Rac-[1(pyPhMeC)_2C_5H_3N]Pd(OAc)]^+$

The title cation is represented below with its ring inversion product. As 1H nmr spectra do not distinguish molecules related by a mirror plane the *S,S* enantiomer has been omitted for clarity.



It is clear that (B) and (B') would be expected to give rise to distinguishable ^1H nmr spectra. In (B), a methyl environment of similar chemical shift to the free ligand would be expected, while in (B') this resonance would be expected to shift downfield due to the proximity of the metal center.¹⁴ In the instance of an approximately equal distribution between the available conformers a spectrum similar to that of the *meso* complex would be expected, i.e., the spectrum would represent the sum of complexes having methyl groups near to, and far from, the metal center.

The palladium(II) complexes of simple bi- and tridentate triarylmethane ligands, and the extended ligands, share the structural feature shown below.



Molecular models suggest that when R and R' are of equivalent molecular dimensions R' experiences greater steric crowding than R. This is supported by the X-ray structural results for some related gold(III) complexes (see pages 15 and 17), and for the palladium(II) complexes illustrated on pages 51, and 52. In each case an uncoordinated pyridine or phenyl group resides above the metal atom, with the smaller methine hydrogen atom residing between chelating aromatic groups.

However, for the title complex, with methyl and phenyl substituents on the bridging carbon atom, molecular models do not readily suggest which substituent would exert the greatest steric demand. The "diameter" of a methyl group is approximately 4.0 Å while the "thickness" of a phenyl group is approximately 3.4 Å.²⁶

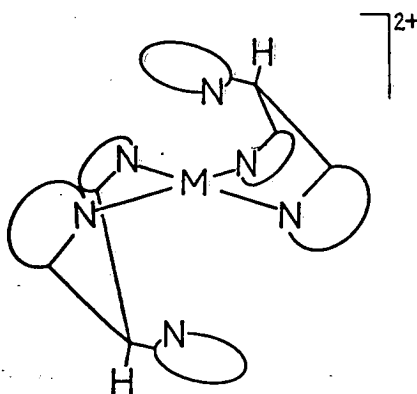
The ^1H nmr spectrum of the title complex is very similar to the ^1H nmr spectrum of the preceding *meso* complex. Within the region containing resonances associated with methyl and acetate groups, two methyl and two acetate resonances are observed. Thus, both equatorial and axial methyl groups are present.

Considering the conformations available to the *racemic* complex, both are assumed to be present in approximately equal ratio (from integration). As the aromatic region of the ^1H nmr spectrum is also very complicated with extensive overlap of resonances, due to the presence of conformational equilibrium, further investigation of this complex was not attempted.

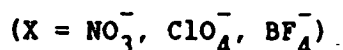
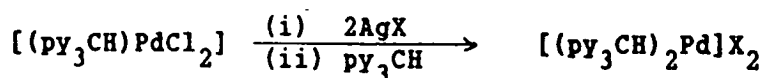
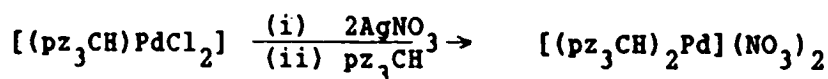
2.5 Synthesis and Structural Studies of Palladium(II) Complexes of Tripodal N-Donors.

The tripodal polydentate N-donor ligands tris(pyridin-2-yl)methane, (py_3CH), tris(pyrazol-1-yl)methane, (pz_3CH), and tris(pyrazol-1-yl)borate, (pz_3BH) $^-$, have also been used to investigate the coordination behaviour of Pd(II). Cations of the type $[\text{L}_2\text{Pd}]^+$ ($\text{L} = \text{py}_3\text{CH}$ and pz_3CH) and the neutral complex $[(\text{pz}_3\text{BH})_2\text{Pd}]$, have been prepared to assess the potential for PdN_4 to extend its coordination sphere in the solution and solid states.

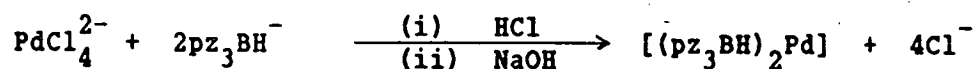
The ligands offer differences in geometry and basicity with square-planar geometry for palladium achieved through bidentate coordination of the ligands, and possible higher coordination achieved by axial donor interaction.



Cations of the formulation $[\text{L}_2\text{Pd}]^{2+}$ have been derived from the chloro-complexes $[\text{LPdCl}_2]$, previously described (page 24), by reaction with silver salts and a further mole equivalent of ligand (see Experimental, page 184).



The neutral complex $[(pz_3BH)_2Pd]$ was obtained directly by reaction of tetrachloropalladate(II) with tris(pyrazol-1-yl)borate.

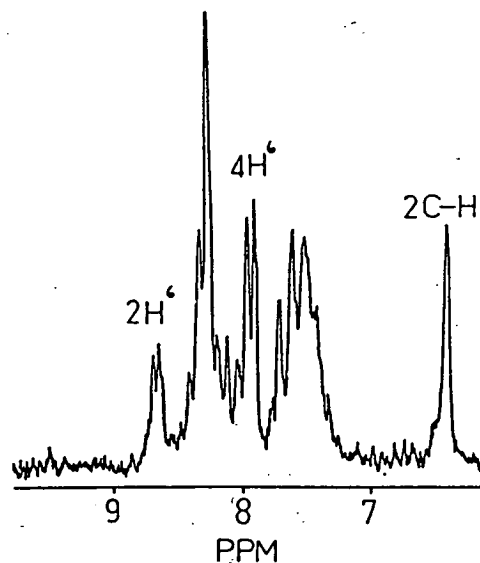


The complexes have appropriate microanalysis, infrared spectra consistent with presence of ligand, and appropriate oxyanion or BF_4^- absorptions. Conductivities for the salts are consistent with 1:2 electrolytes.

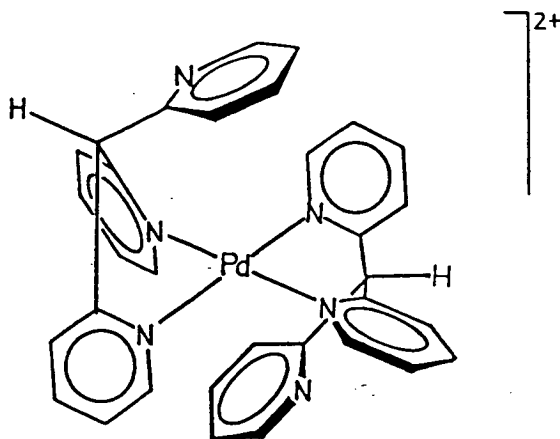
A number of salts containing different anions were prepared to obtain a complex of the cation $[(py_3CH)_2Pd]^{2+}$ of suitable crystallinity for X-ray structural study. For this purpose the tetrafluoroborate salt was found to be the most satisfactory.

2.5(i) ^1H nmr (100 MHz) Characterisation of the Complex
 $[(\text{py}_3\text{CH})_2\text{Pd}](\text{NO}_3)_2$

In D_2O at ambient temperature the complex $[(\text{py}_3\text{CH})_2\text{Pd}](\text{NO}_3)_2$ exhibits a complex spectrum in the aromatic region, consistent with the presence of more than one pyridine ring environment.



In the downfield region of the spectrum one H(6) environment (8.84 ppm, 2H, $J(\text{H}(6,5))$ 5Hz) is readily assigned with the other H(6) environment less certain, due to resonance overlap, but appearing to occur at 8.16 ppm (4H, $J(\text{H}(6,5))$ 5Hz). These observations are consistent with the expected consequences of interligand anisotropic shielding if two pyridine groups are uncoordinated, as the effects are similar to the shielding caused by uncoordinated pyridine donors in the ^1H nmr spectrum of $[(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}]\text{Pd}(\text{OAc})](\text{OAc})$ (see page 34). This effect, and the steric bulk of the uncoordinated donors compared with the bridgehead hydrogen atom suggest the ligand orientation below. An orientation such that the uncoordinated donors are remote from the metal is unlikely due to the reasons previously discussed on page 45.



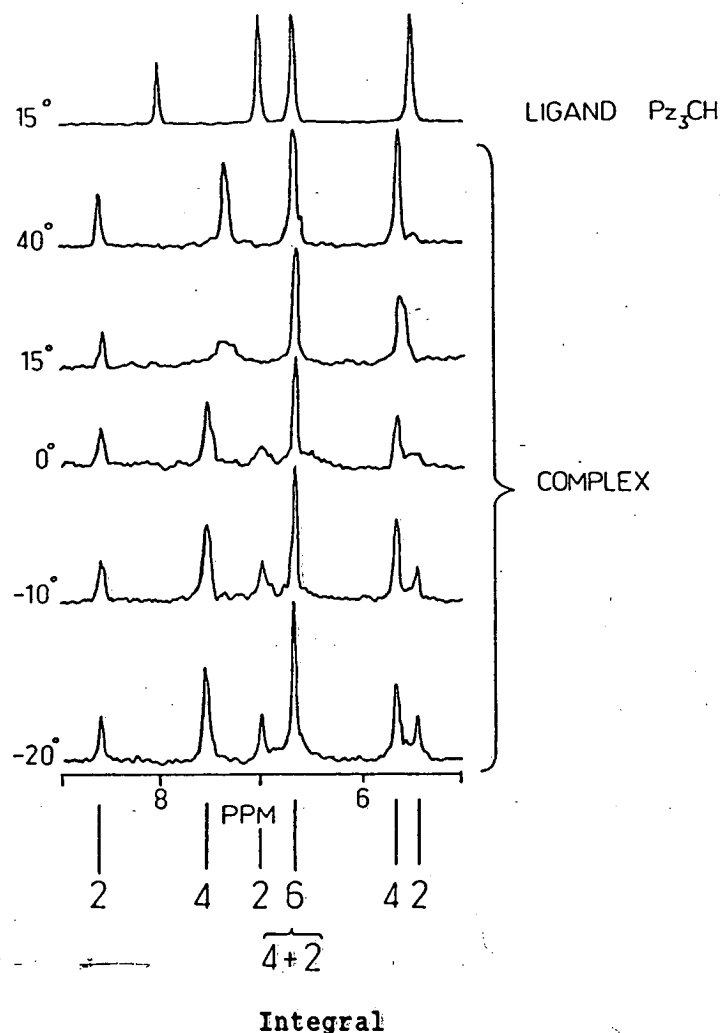
On heating ($> 30^{\circ}\text{C}$) the aromatic region of the spectrum undergoes simplification to give two very broad resonances at ca. 8.7 - 8.0 (18H) and 7.8 (6H) ppm. The variable temperature ^1H nmr spectra are thus consistent with the presence of rapid equilibria between donor ring environments in the square-planar PdN_4 group and uncoordinated and/or weakly coordinated environments.

2.5(ii) ^1H nmr (100 MHz) Characterisation of the Complexes $[(\text{pz}_3\text{CH})_2\text{Pd}](\text{NO}_3)_2$ and $[(\text{pz}_3\text{BH})_2\text{Pd}]$

In the ^1H nmr spectra of the title complexes containing tripodal pyrazole-based ligands resonances attributable to H(3-5) and C-H are observed but the borate proton in pz_3BH^- is not observed due to nuclear quadrupole broadening.

Both $[(\text{pz}_3\text{CH})_2\text{Pd}](\text{NO}_3)_2$ and $[(\text{pz}_3\text{BH})_2\text{Pd}]$ show simple spectra at ambient temperature of four and three broadened resonances, respectively. The complexes exhibit sharpened H(3-5) resonances at lower temperatures (-20°C or below), in CD_3OD and CDCl_3 respectively, with resonances in the ratio 4:2:6:4:2 (pz_3CH) and 4:2:2:4:6 (pz_3BH^-), consistent with two pyrazole ring environments in 2:1 ratio. For example, the variable temperature spectrum of $[(\text{pz}_3\text{CH})\text{Pd}](\text{NO}_3)_2$ is shown below. In this spectrum the integration ratio obtained at low temperature is consistent with the ratio $4\text{H}:2\bar{\text{H}}:4\text{H}+2\bar{\text{H}}:4\text{H}:2\bar{\text{H}}$, where H and $\bar{\text{H}}$ represent protons from differing pyrazole ring environments.

A similar result is observed for the complex $[(\text{pz}_3\text{BH})_2\text{Pd}]$ in CDCl_3 at low temperature, and thus, all complexes show facile exchange between coordinated and uncoordinated ring environments.

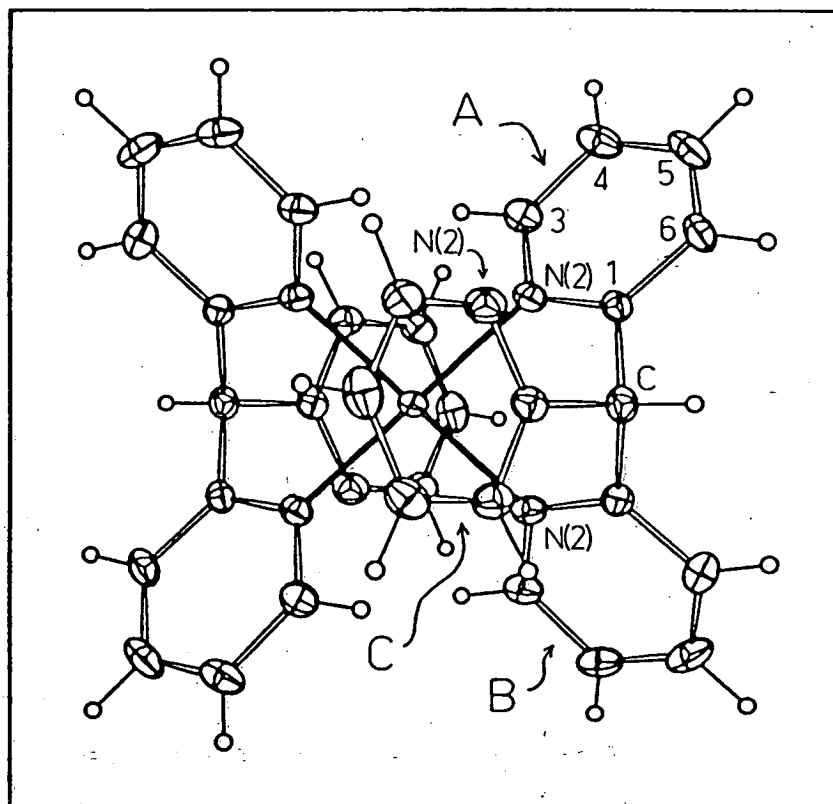


2.5(iii) Solid State Structures of $[(py_3CH)_2Pd](NO_3)_2$, $[(pz_3CH)_2Pd](BF_4)_2$ and $[(pz_3BH)_2Pd]$.²⁵

Aspects of the molecular geometry about palladium in the complexes are shown on the following pages. The ionic complexes are isomorphous.

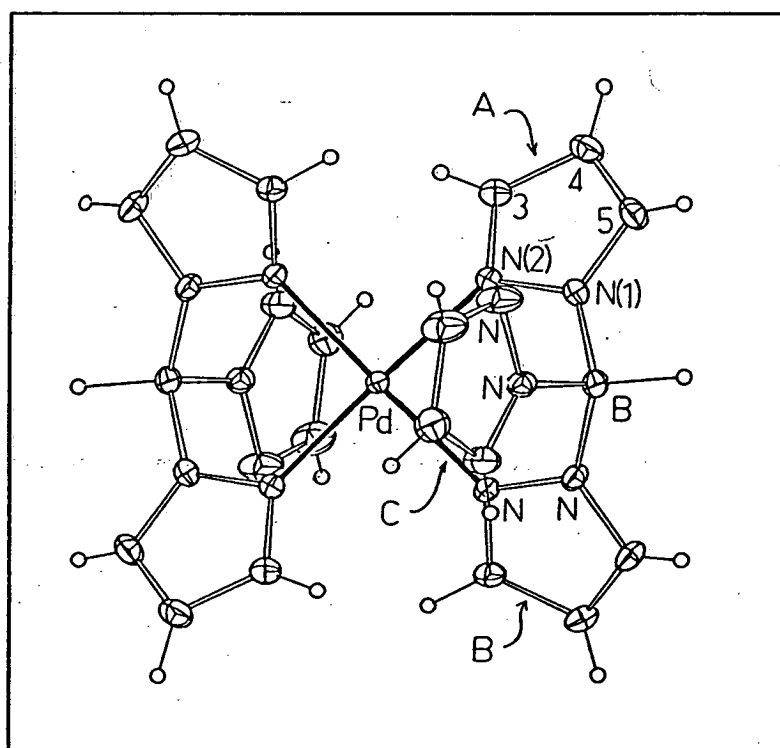
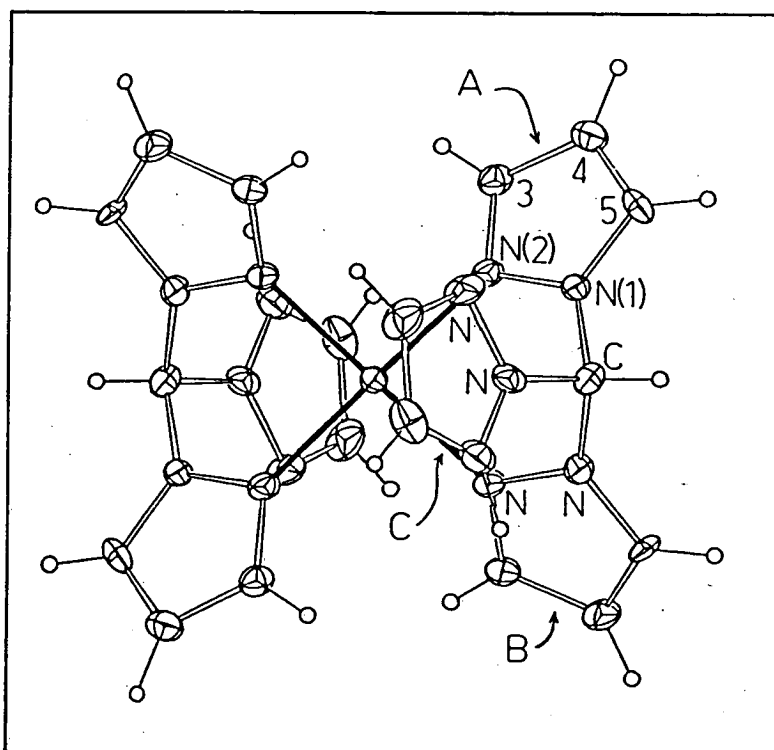
The pyridine and pyrazole rings are planar with maximum deviation from a mean plane observed for C(4) (0.022\AA) in ring C of the complex containing py_3CH . The apical carbon and boron atoms are also close to the projected ring planes with a maximum deviation of 0.199\AA for boron from ring C of $[(pz_3BH)_2Pd]$. Nitrate and tetrafluoroborate ions are regular (within 3σ in bond lengths and angles).

All three complexes have square-planar geometry for the palladium atom (bold lines) with the metal atoms at



The cation
 $[(py_3CH)_2Pd]^{2+}$
 from its nitrate
 salt

crystallographic centers of symmetry. The ligands are present as *N,N*-bidentate donors with Pd-N bond lengths in the range 1.987(8) - 2.029(4) Å, intraligand N-Pd-N angles 87.0(1) - 90.1(1)°, and interligand N-Pd-N angles 89.9(1) - 93.0(1)°. The coordinated rings are inclined to the PdN₄ plane, with dihedral angles between aromatic ring and PdN₄ planes of 44.6° (ring A) and 45.0° (ring B) for the py₃CH complex, 36.8° and 39.9° for the pz₃CH complex, and 37.2° and 37.6° for the pz₃BH⁻ complex. The uncoordinated rings above the PdN₄ planes form dihedral angles of 45.0° (py₃CH), 51.0° (pz₃CH) and 58.1° (pz₃BH⁻).



2.6 Conclusions

The Lewis acidity of the palladium atom in the ' PdO_2N_2 ', ' PdON_3 ', and ' PdN_4 ' kernels is clearly very low toward the nitrogen donor ligands studied. However, variable temperature ^1H nmr spectra of the complexes containing uncoordinated axial pyridine and pyrazole groups indicate facile interconversion of coordinated and uncoordinated environments for the donor rings, consistent with intramolecular processes involving 5-coordinate intermediates.

Structures determined by X-ray crystallography, and those deduced from ^1H nmr spectra indicate that steric demand between coordinated bidentate donors plays an important role in the orientation adopted by ligand substituents.

For this type of study complexes of palladium(II) acetate have been found to be of greater use than analogous chloro-complexes due to the high solubility and crystallinity of the products. For ^1H nmr spectroscopic studies the use of two dimensional COSY spectra has been found to be invaluable for otherwise difficult proton assignments, and is particularly well suited to the study of pyridine containing ligands.

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CHAPTER THREE

SOME CYCLOPALLADATION REACTIONS OF SIMPLE AND EXTENDED LIGANDS WITH PALLADIUM(II) ACETATE.*

3.1 Introduction

Cyclometallation reactions, in which aryl metal-carbon σ -bonds are formed by replacement of ortho-hydrogen atoms by metal atoms to yield organometallic intramolecular coordination compounds, have been an object of increasing general interest over recent years. A number of reviews have been published on this subject and these are usually divided on the basis of the type of donor heteroatom present in the cyclometallated product, for example, nitrogen¹, phosphorus², sulfur³, and arsenic⁴. Complexes arising from such cyclometallation reactions have been used in regiospecific organic syntheses⁵, in preparation of complexes containing metal-metal bonds⁶, and in producing, for example, hydrido-bridged complexes⁷.

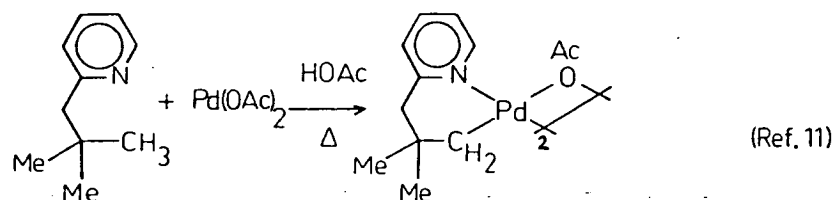
The range of metal substrates that undergo cyclometallation is very wide¹⁻⁴ and there are probably several mechanisms for the reactions dependent on both the metal and ligand. For low valent metals such as Ir(I) and Rh(I) the reaction is presumed to proceed *via* intramolecular oxidative addition⁸, whereas for cyclopalladation it has generally been accepted that metal-carbon σ -bonds are formed by electrophilic attack on the aromatic ring by the metal⁹.

A large number of ligands containing Group V or VI donor atoms have been metallated using palladium acetate as the starting material, and generally, where a choice of position of attack exists, the formation of a five-membered ring is favoured^{9a}. However, 4-membered ring formation is known for phosphines¹⁰, and examples of 6-membered rings containing N-donors are becoming increasingly common.¹¹

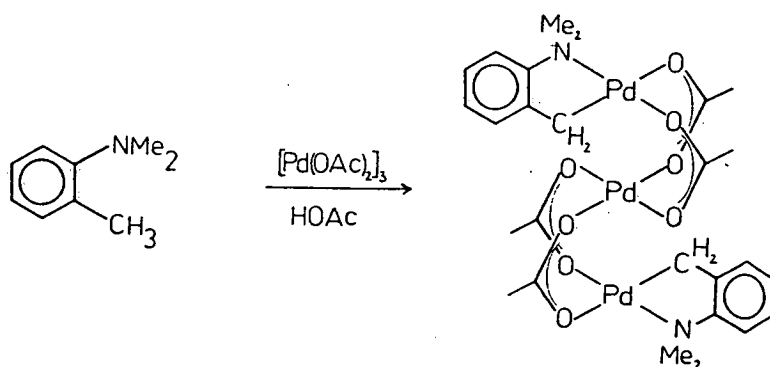
In most instances the products from metallation by $\text{Pd}(\text{OAc})_2$ are dinuclear molecules with two acetato-bridging units between

* Some published material concerning this topic appears in Publication 4 page 228.

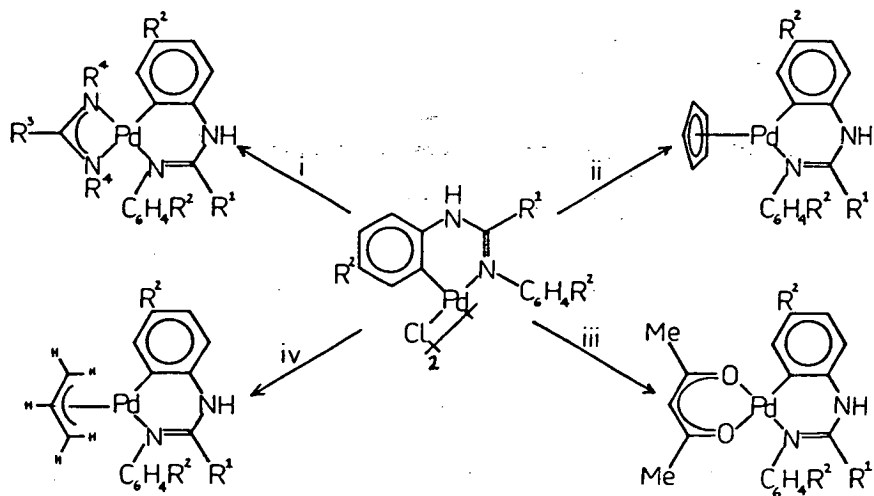
the palladium atoms, for example,



However, some exceptions are known where, for example, metallation of a ligand by (trimeric) palladium acetate has recently been reported to give a trinuclear species¹².



To simplify spectral interpretation (i.e. to eliminate some conformational effects) and to improve solubility properties of such complexes a range of "bridge-splitting" reagents have been employed, usually on the bridged chloro- complexes derived by metathesis from the acetato- complexes with sodium or lithium chloride. The scheme below (from ref. 13) illustrates some typical derivatives.



i) $\text{Li}(\text{N}(\text{R}^1)\text{C}(\text{R}^2)=\text{NR}^3)$, ii) NaC_5H_5 , iii) $\text{Ti}(\text{acac})_3$, iv) $\text{C}_5\text{H}_5\text{MgCl}$

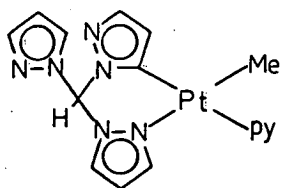
(ref. 13)

As previously mentioned (page 3), other derivatives of this type of organopalladium compound may be prepared by insertion of small unsaturated molecules into the metal-carbon bond.

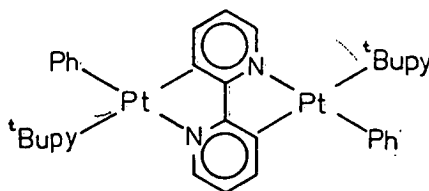
Cyclopalladation involving arylalkyl- or arylpyridine containing ligands may result in formation of 6- or 5-membered palladocycles, for example, reaction of palladium acetate with 2-benzylpyridine, pyPhCH_2 , gives $[(\text{pyCH}_2\text{C}_6\text{H}_4\text{-}N, C^2)\text{Pd}(\mu\text{-O}_2\text{CMe})]_2^{14}$, and $[\text{PdCl}_4]^{2-}$ reacts with 2-phenylpyridine to give $[(\text{pyC}_6\text{H}_4\text{-}N, C^2)\text{Pd}(\mu\text{-Cl})]_2^{15}$.

Closely related polydentate ligands usually give coordination compounds rather than metallation products, thus, 2,2'-bipyridyl gives a product resulting from normal *N,N*-bidentate coordination on reaction with $[\text{PdCl}_4]^{2-}$.¹⁶

However, metallation of the polydentate ligand 2-(2-thienyl)pyridine¹⁷, and 2,2'-bipyridyl with iridium(III)¹⁸, were reported in 1979 and 1981, respectively. Soon after, metallation of the tripodal tridentate ligand tris(pyrazol-1-yl)methane from its *N,N*-chelate complex with dimethylplatinum(II) in hot pyridine was reported¹⁹, followed by reports on dimetallation of 2,2'-bipyridyl from its *N,N*-chelate complex with diphenylplatinum(II) in hot 4-*t*-butylpyridine²⁰.



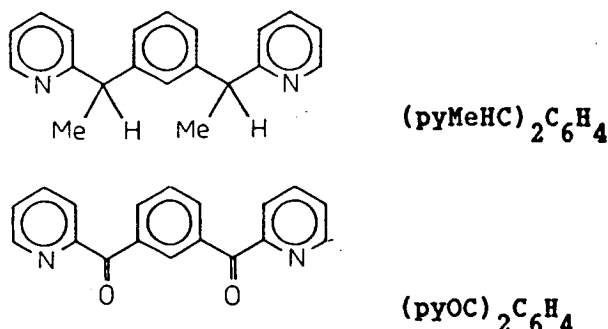
Ref. 19



Ref. 20

As some potentially bi- and tridentate *N*-donor heterocyclic ligands have been shown to cyclometallate forming *N,C*-chelates, as opposed to adopting the more usual *N,N*-coordination mode, an examination has been made of the reaction of the simple and extended pyridine-based ligands, $\text{py}_n\text{Ph}_{3-n}\text{CH}$ ($n=1-3$), $\text{py}_n\text{CH}_{4-n}$ ($n=2,3$), *meso*- and *rac*-(pyPhMeC)₂ $\text{C}_5\text{H}_3\text{N}$, (py_2MeHC)₂ $\text{C}_5\text{H}_3\text{N}$, (pyMeHC)₂ C_6H_4 , and (pyOC)₂ C_6H_4 with $\text{Pd}(\text{OAc})_2$ in acetic acid. The structures of those ligands possessing a disubstituted benzene

ring are shown below. The other ligands have been illustrated in the preceding chapter (pages 18, 27).



3.2 Simple Ligands; $\text{py}_n\text{Ph}_{2-n}\text{CH}_2$ ($n = 1, 2$), $\text{py}_n\text{Ph}_{3-n}\text{CH}$ ($n = 1-3$) and py_3PhC .

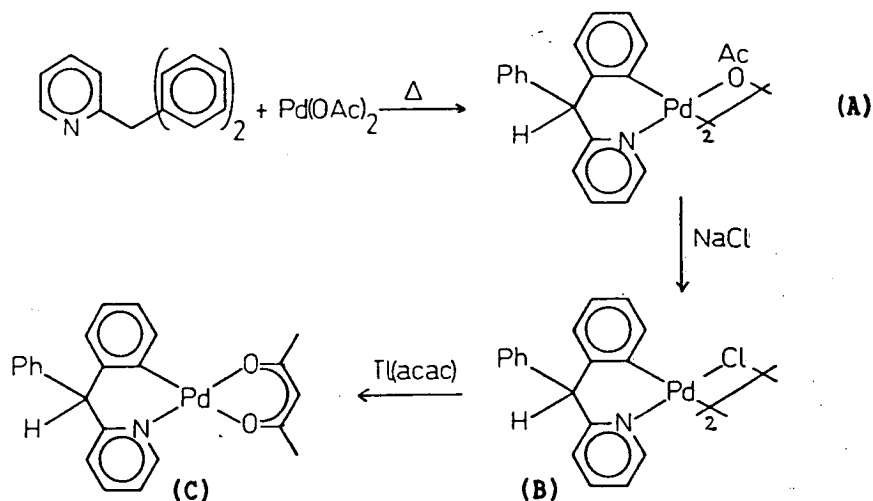
Attempts to form cyclopalladated products of the simple ligands were made by dissolving equimolar quantities of ligand and $\text{Pd}(\text{OAc})_2$ in glacial acetic acid and heating at or near reflux temperature ($100-118^\circ\text{C}$). Product isolation was initially attempted by removal of reduced palladium (if any) by filtration, removal of acetic acid by rotary evaporation (ca. 17 mm), further drying under reduced pressure with gentle heating (0.1 mm, $60-70^\circ$), followed by normal crystallisation methods from organic solvents. Although this method was satisfactory in some instances, traces of acetic acid usually remained.

To facilitate ^1H nmr spectral analysis of crude products the procedure was slightly modified. The product resulting from rotary evaporation and vacuum drying was taken into either CHCl_3 or CH_2Cl_2 and treated with a saturated aqueous solution of sodium carbonate. On isolation of the organic phase, drying, and removal of solvent under vacuum, the crude product freed of all traces of acetic acid was obtained.

Comparison of ^1H nmr spectra of the free ligand and nitrogen-donor coordination complex with the crude product was then used, together with T.L.C. analysis, to determine if metallation had occurred. Characteristically, on metallation two features are evident - a reduction in the ligand (in complex): acetate ratio occurs in comparison with the normal coordination complex, and separation of the aromatic resonances resulting from

the lower symmetry induced by *N,C*- rather than *N,N*-coordination is observed.

Thus, for the ligands py_2CH_2 , $\text{py}_n\text{Ph}_{3-n}\text{CH}$ ($n=1-3$) and py_3PhC , only pyPh_2CH was found to cyclometallate in a similar manner to that found for 2-benzylpyridine.¹⁴ Both chloro- and acetylacetonato- derivatives were obtained to assist with spectral interpretation.



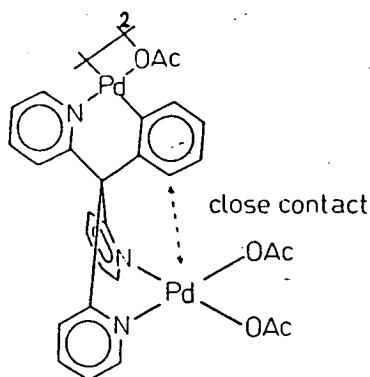
For (A) the I.R. spectra exhibit acetato- bands at 1586 and 1416 cm^{-1} , consistent with the dimeric structure shown and at similar positions to those found for the dimeric palladated complex of 2-benzylpyridine (1585 cm^{-1} , 1420 cm^{-1}).¹⁴ Unambiguous assignment of these absorptions has been made possible by comparison with the chloro- complex (B).

The more soluble acetylacetonato- complex (C) exhibits ^1H nmr resonances for acac protons, including two methyl environments, single resonances for pyridine $\text{H}(6)$ and methine protons, and complex multiplets for the phenyl and remaining pyridine resonances.

Under similar conditions, reaction of py_2CH_2 , py_2PhCH , py_3CH , and py_3PhC with $\text{Pd}(\text{OAc})_2$ gave only the *N,N*-chelate complexes $[\text{LPd}(\text{OAc})_2]$ previously described (page 18).

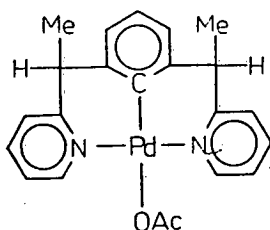
A second reaction of py_3PhC with two equivalents of $\text{Pd}(\text{OAc})_2$ was performed to determine if the uncoordinated ring may direct electrophilic attack on the phenyl substituent. However, in this case a more substantial reduction of palladium was noted and only the *N,N*-chelate complex could be detected. Molecular models

suggest that such attack may be hindered by the ring orientation(s) allowed by the six-membered *N,N*-chelate groups, since an orientation appropriate for metallation may require a close contact as shown below.



3.3 Extended Ligands

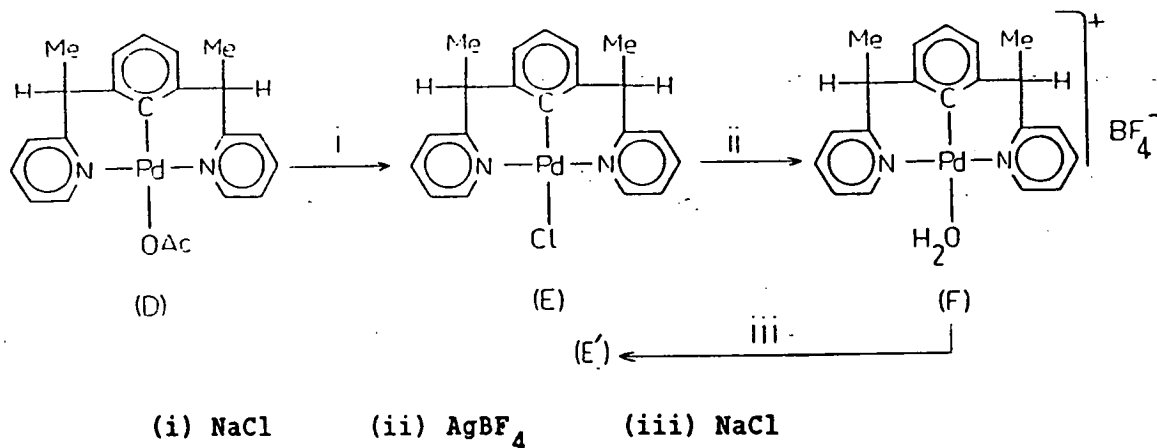
Reaction, as above, of the pyridine-linked extended ligands *meso/rac*-(pyPhMeC)₂C₅H₃N, and (py₂MeC)₂C₅H₃N generated the salts previously described (page 28) with no detected metallation products. Reaction of the benzene-linked ligand (pyMeHC)₂C₆H₄ (*meso/rac* mixture) with Pd(OAc)₂ in acetic acid (100°C, 20h) generated the product below in moderate yield (40-60%).



(D)

The monomeric nature of complex (D) has been established by osmometric molecular weight determination (found 429, calc. 453). Infrared absorptions for the acetato- group at 1596 and 1384 cm⁻¹ are indicative of unidentate coordination, and may be assigned with certainty by comparison with the chloro- complex (E) generated by metathesis with NaCl. Complex (E) has also been used to facilitate ¹H nmr spectral assignment, while complexes (F) and (E') have been prepared to determine if preferential diastereoisomer-selective crystallisation of the salt (F) occurs. The tetrafluoroborate salt, (F), was obtained in 72% yield from

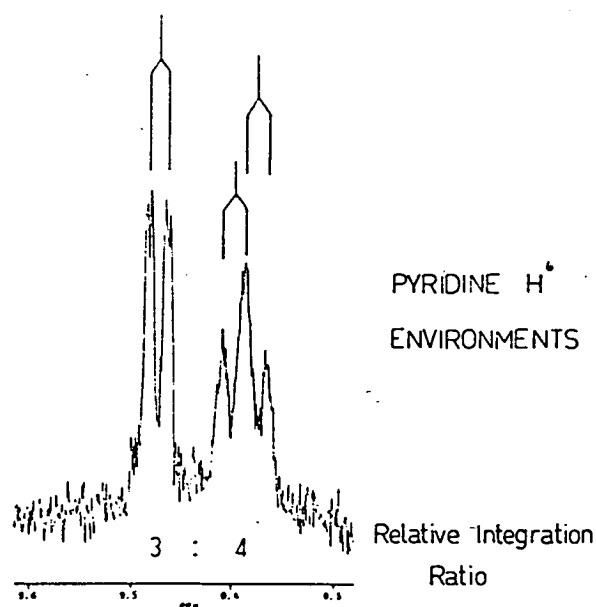
(E). It was converted back to the chloro- complex (E') by quantitative metathesis with aqueous NaCl, as (F) gives a rather poor ^1H nmr spectrum in CDCl_3 .



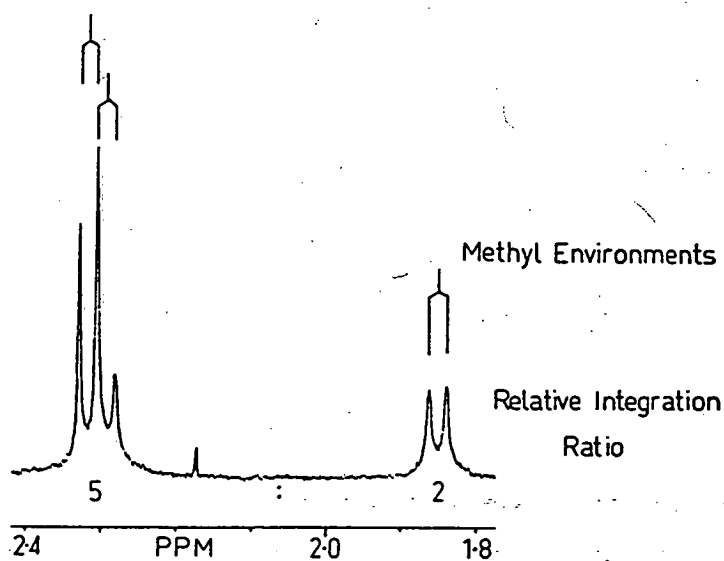
3.3(i) ^1H nmr Characterisation of $[(\text{pyMeHC})_2\text{C}_6\text{H}_3\text{Pd}(\text{X})]$,
 where $\text{X} = \text{OAc}(\text{D})$, and $\text{Cl}(\text{E}, \text{E}')$.

The standard 300 MHz ^1H nmr spectra of complexes (D) and (E), at ambient temperature in CDCl_3 , and the free ligand, are shown on page 65. Comparison between spectra of the complexes allows the acetate resonance of (D) to be assigned to the signal at 2.04 ppm. Both (D) and (E) have complex resonance patterns associated with H(6), methine, and methyl resonances. However, as these are clearer for the chloro- complex (E), this spectrum will be discussed initially.

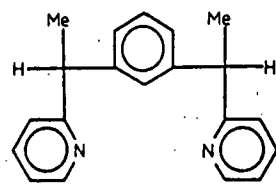
Examination of pyridine H(6) resonances of (E) shows that three chemically distinct H(6) environments are present, one with sharp features and the other two partially overlapping and broadened.



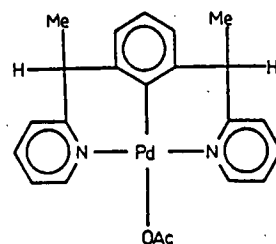
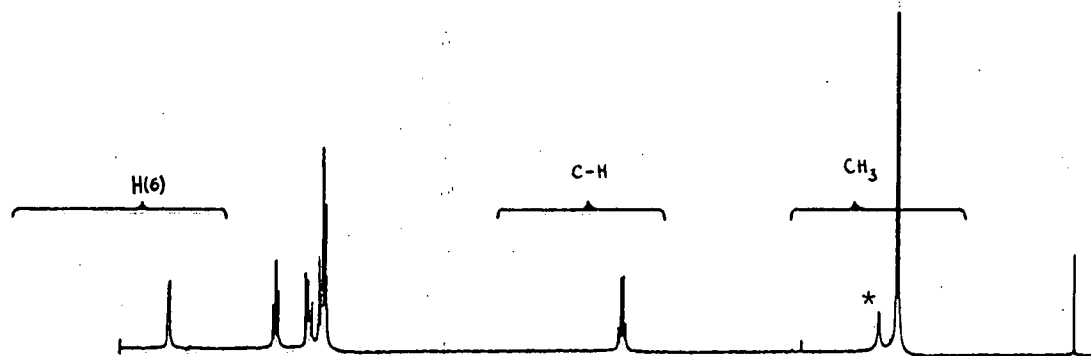
The ligand methyl resonances (doublets) show a similar division into three contributing methyl environments with partial overlap of the downfield resonances and with the lower intensity signals broadened.



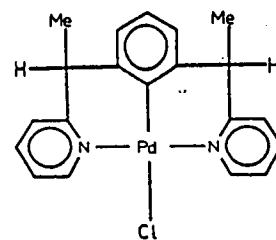
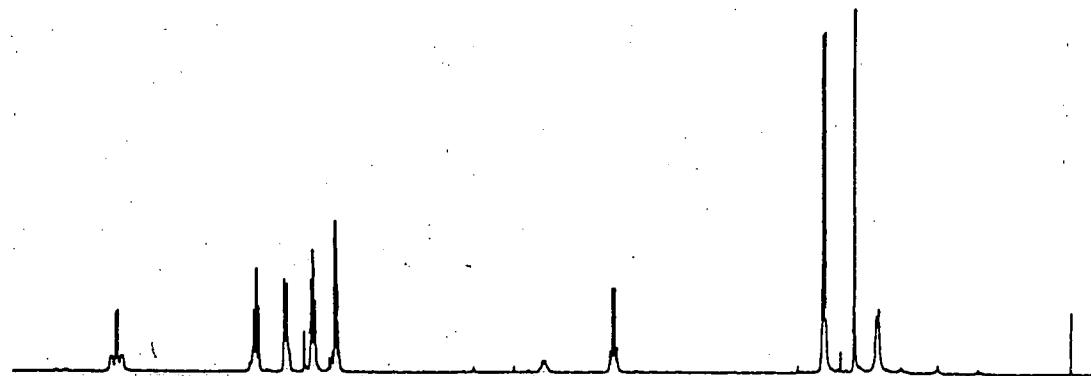
Resonances associated with methine protons (quartets) are divided into two (apparently) with the downfield resonance broadened in comparison with the upfield resonance.



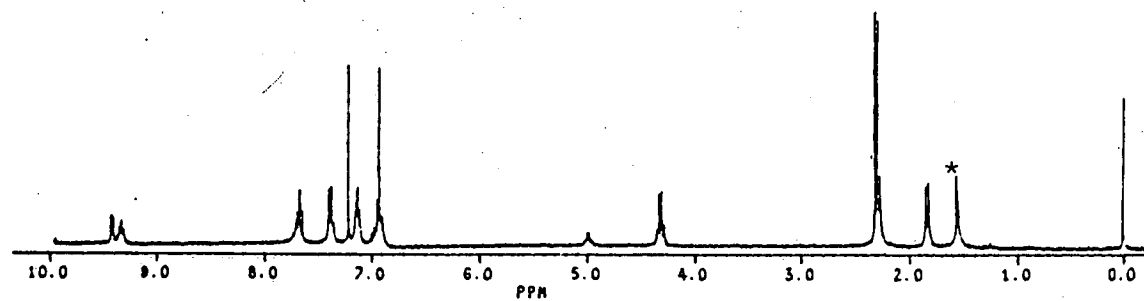
FREE LIGAND



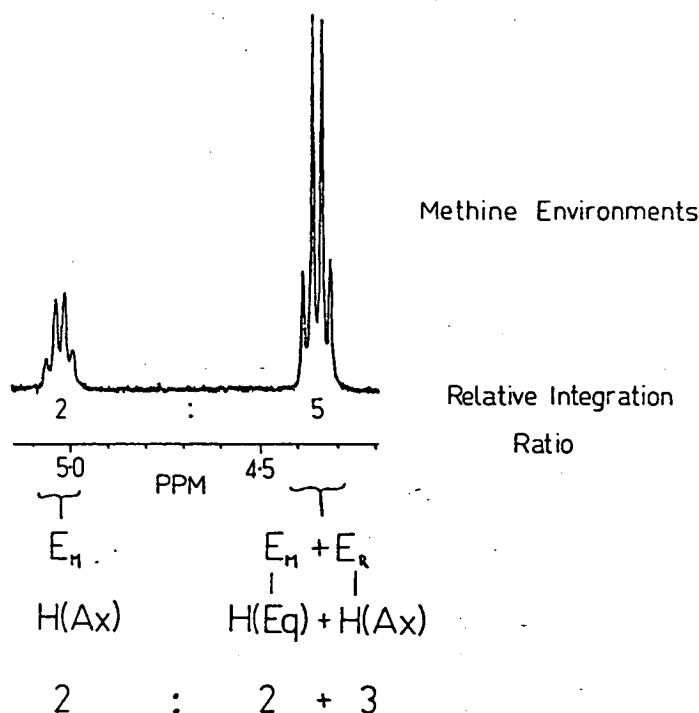
COMPLEX D



COMPLEX E



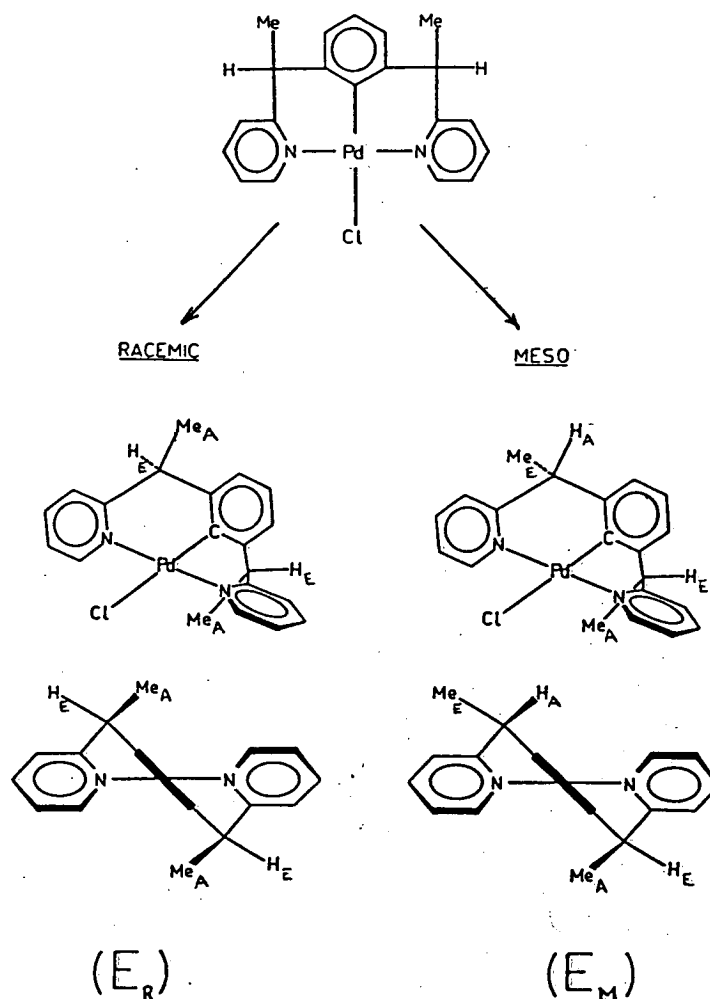
* = H₂O



Comparison with the total integration ratios H(6): CH(methine): CH₃:OAc gives the expected ratio 2 : 2 : 6 : 3. Thus, the upfield methine resonance represents coincident quartets with similar coupling constants. The relative integration ratio for these signals may be re-expressed as 2 : 2+3. Similarly, the methyl group ratio may be expressed as 3+2 : 2.

The division of H(6), CH, and CH₃ resonances may be rationalised in terms of the presence of a mixture of *meso* and *racemic* complexes in ca. 4:3 ratio, respectively. The representations of these complexes, below, are similar to those used in previous discussion (page 33), and that discussion relates directly to these structures.

(E)

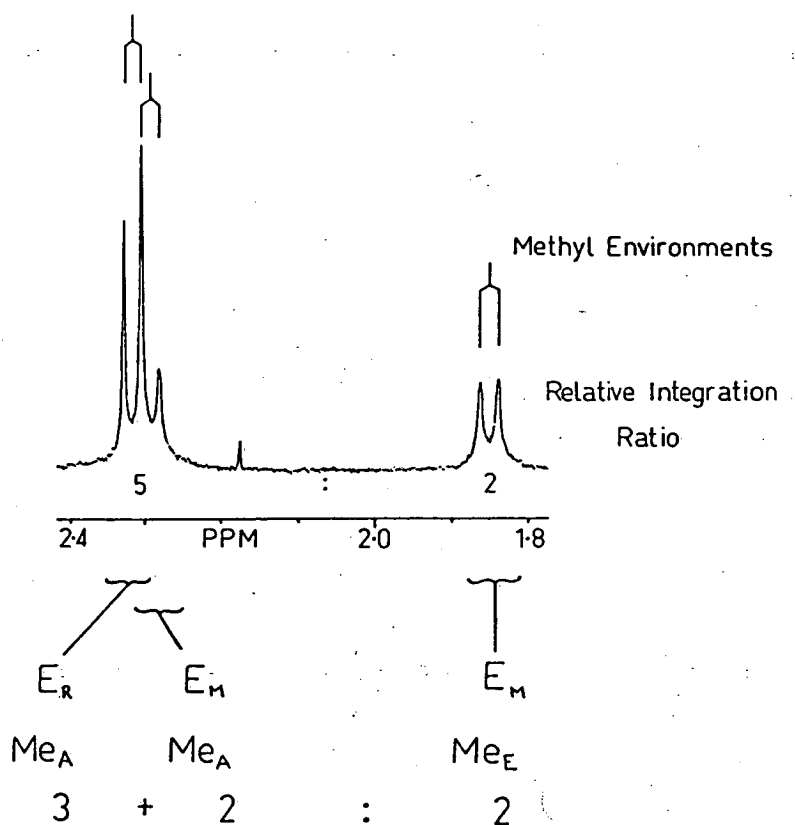


For the *racemic* complex (E_R), the ligand conformation adopted is expected to be that depicted due to the greater steric bulk of the methyl group compared with that of the methine hydrogen atom, and ring inversion would not be expected (see page 45). The complex would be anticipated to give rise to one resonance for each pyridine H(6), CH, and CH₃ environment. The methine protons would be expected to display a similar chemical shift to those in the free ligand, while the methyl groups would be expected to resonate further downfield due to their proximity to the metal center.

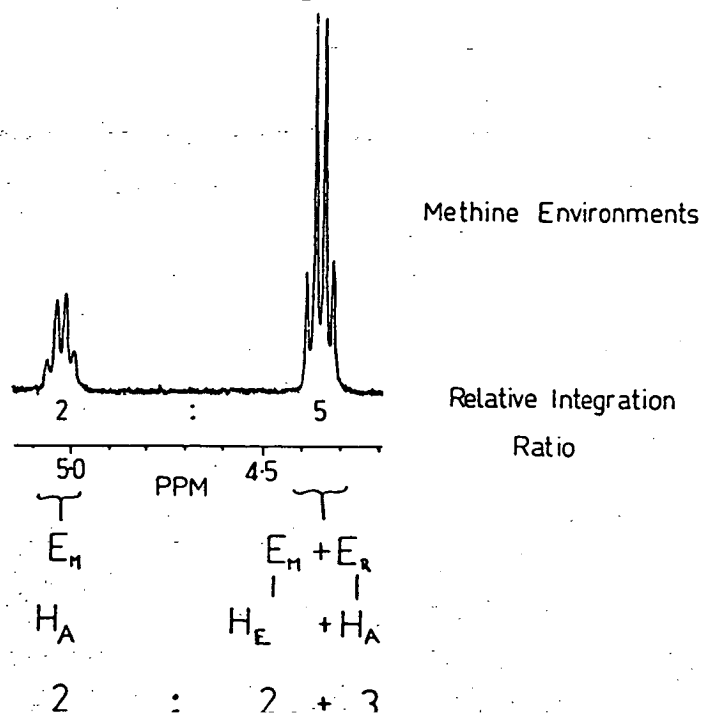
For the *meso* complex (E_M) two signals would be expected for each H(6), CH, and CH₃ protons as all are in chemically inequivalent environments. Methine and methyl environments would

be expected to each be composed of one resonance similar to the free ligand and one shifted downfield.

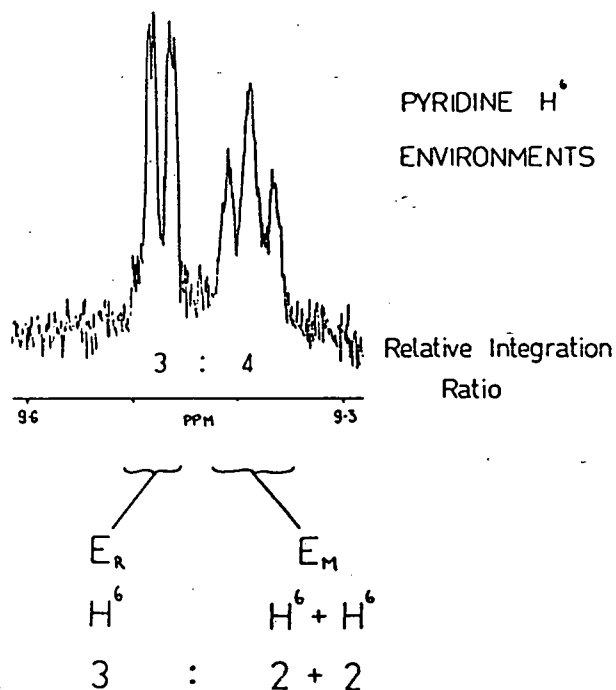
Thus, the observed methyl resonances may be divided into contributions from $E_R(\text{Me}_A)$ and $E_M(\text{Me}_A \text{ and } \text{Me}_E)$, in ca. 3:4 ratio.



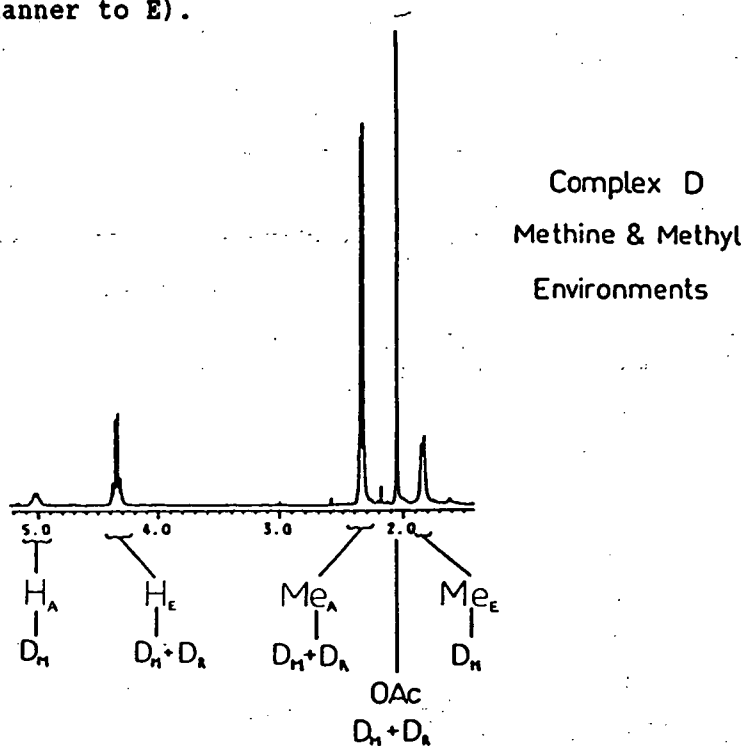
Similarly, the observed methine and pyridine H(6) environments may be divided into contributions from E_R and E_M , but assignment of the individual H(6) contributions from E_M cannot be made with certainty.



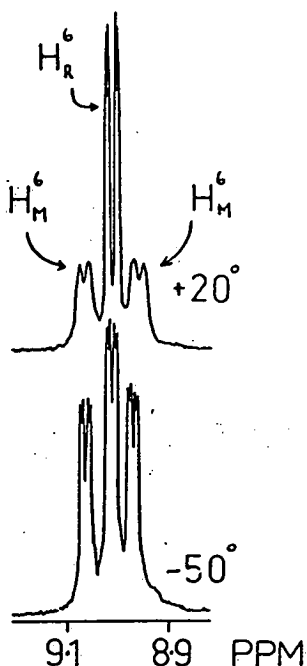
Line broadening in resonances associated with E_M is presumably attributable to ring inversion processes (similar to those illustrated on page 33). Assignment of other aromatic resonances is discussed on page 71.



The 1H nmr spectrum of the acetato- complex (D) is very similar to (E). In the region 5.5 - 1.5 ppm, shown below, the contributions to methine, methyl and acetato-(methyl) resonances can be seen. However, for this complex exact coincidence of resonances accounts for the assignments given, (deduced in an analogous manner to E).



At ambient temperature H(6) resonances of (D) appear as one sharp resonance flanked by two broadened resonances. On lowering of temperature the broadened resonances sharpen and are asymmetrically placed about the central resonance position. At $+50^{\circ}$ the three H(6) resonances collapse to one broadened signal. However, at this temperature resonances associated with methine and methyl groups of the *meso* complex show line broadening, but coalescence, i.e. the averaging of H_A and H_E , and Me_A and Me_E signals by ring inversion, is not observed.

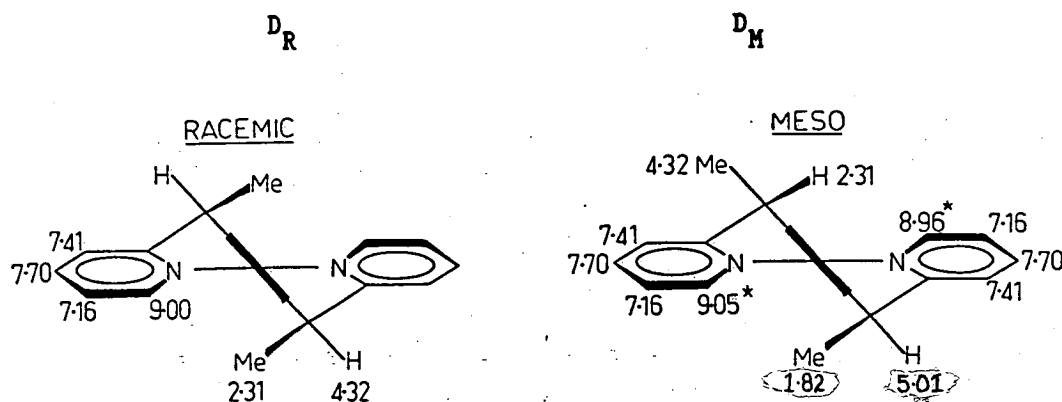


The tetrafluoroborate salt, (F), obtained from (E) by reaction with AgBF_4 , gave a poor quality ^1H nmr spectrum in CDCl_3 . The salt was converted back to the chloro- complex (E') to ascertain if any diastereoisomer selectivity in crystallisation had occurred similar to, for example, *meso*- $[(\text{pyPhMe})_2\text{C}_5\text{H}_3\text{N}]\text{Pd}(\text{OAc})](\text{OAc})$ (page 180). The isomer ratio deduced from methine and methyl resonance integration indicated that no enhancement in proportion of any isomer had occurred.

3.3(ii) The COSY Spectrum of $[(\text{pyMeHC})_2\text{C}_6\text{H}_3]\text{Pd}(\text{OAc})$,
Complex (D).

To establish with greater certainty the identity of individual aromatic resonances and to confirm connectivity within the aliphatic groups COSY spectra of these regions have been obtained (page 72 and 73).

Using the method previously described to deduce connectivity (page 36) the following assignments have been made for the *meso* and *racemic* complexes.

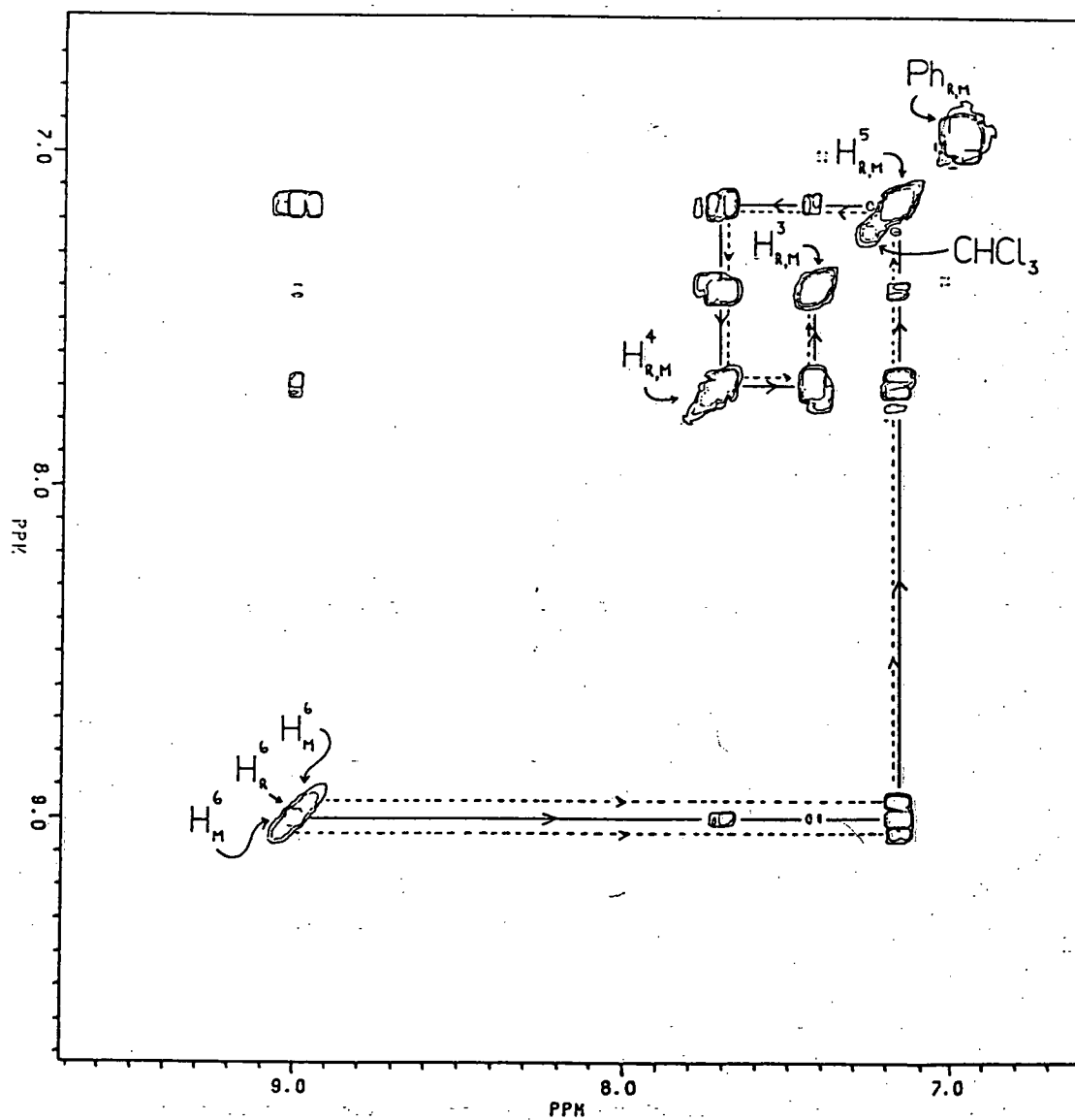


Phenyl and Acetate resonance at 697 and 205 ppm, respectively.

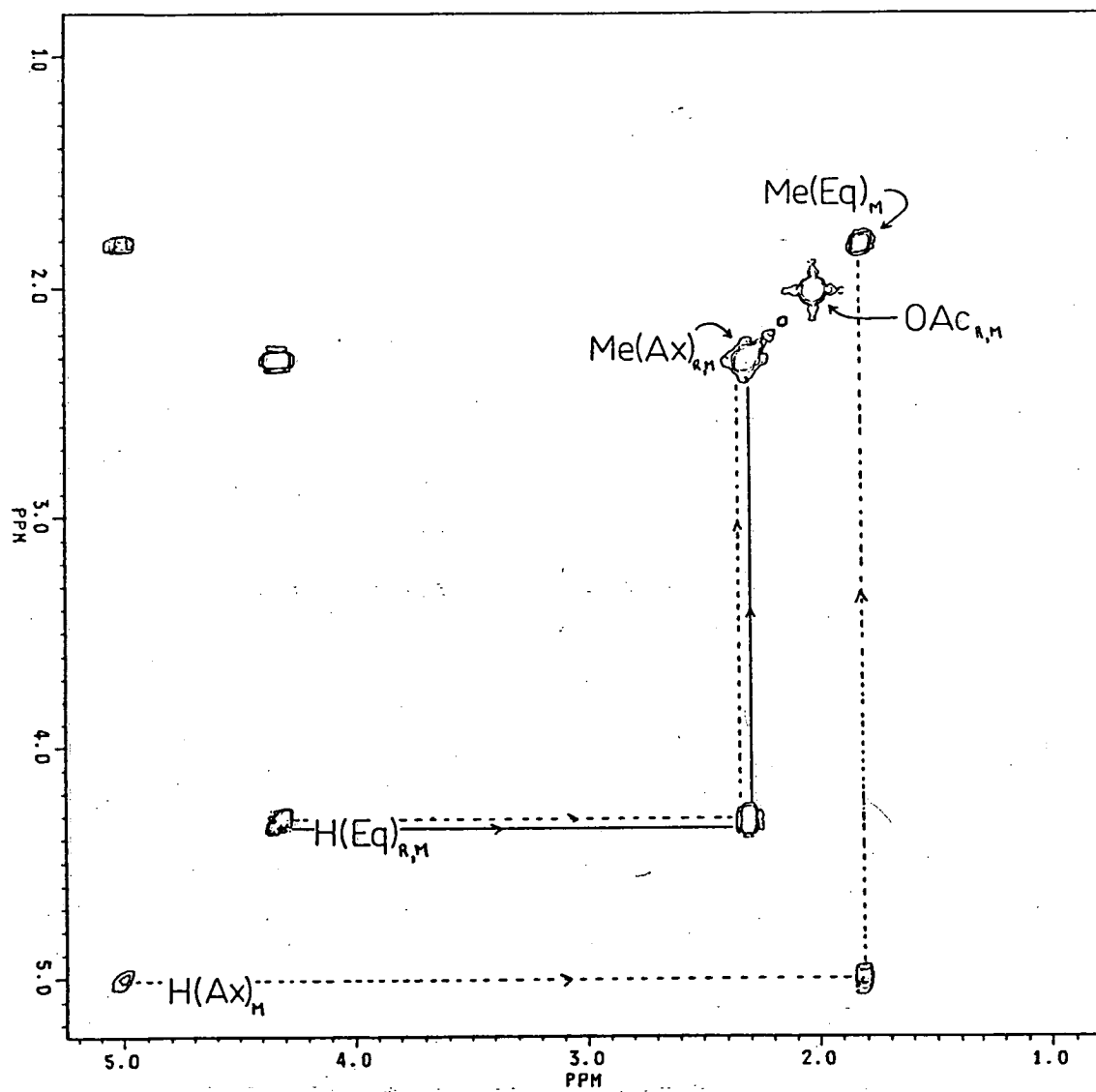
* values may be transposed

Thus, the two diastereoisomers have indistinguishable H(3-5), phenyl, and acetate environments, but are distinguishable from resonances arising from H(6), CH, and CH_3 groups. In the *meso* complex, D_M , two H(6) resonances are observed but the individual assignment of these resonances cannot be made with certainty.

Aromatic Region of Complex D.



Aliphatic Region of Complex D.



3.3(iii) The Solid State Structure of $Meso-[(pyMeHC)_2C_6H_3]Pd(OAc)] \cdot 1.5H_2O$ ²¹

Crystals of the title complex were obtained by dissolution of a sample (*meso/racemic* mixture) in dichloromethane/acetone (1:1) and diffusion of diethyl ether vapour in a sealed chamber.

Aspects of the geometry of the complex are given in Table 3.1 and the molecule is shown overleaf. Neighbouring molecules are related by inversion centers²² (space group $C2/c$), and thus the crystal is composed of the *meso* form of the complex (i.e. *R,S* and *S,R* enantiomers).

The palladium atom has a square-planar coordination environment with the nitrogen donor ligand present as an anionic planar - tridentate (*N,C,N*), with $N(n1)-Pd-C(21)$ angles $88.4(2)^\circ$ ($n=1$) and $88.5(2)^\circ$ ($n=3$), and with $O-Pd-N(n1)$ angles $89.7(2)^\circ$ ($n=1$) and $93.4(2)^\circ$ ($n=3$). The palladium atom lies close to the projected mean planes of the aromatic rings with the greatest deviation observed for ring 3 with a deviation of 0.065 \AA .

The pyridine and phenyl rings are planar, with rings 1, 2, and 3 having χ^2 2.3, 9.2, and 19.0, respectively. Rings 1, 2, and 3 subtend dihedral angles of 47.0° , 39.4° , and 38.6° , respectively, to the plane defined by ' N_2CO '. Comparison between the dihedral angles subtended by the terminal aromatic rings to the plane ' N_2CO ' demonstrates that the equatorial methyl site (between 1 and 2) is more sterically encumbered than the axial methyl site (between 2 and 3).

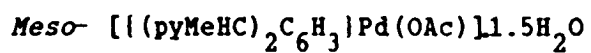
Table 3.1

Palladium Environments

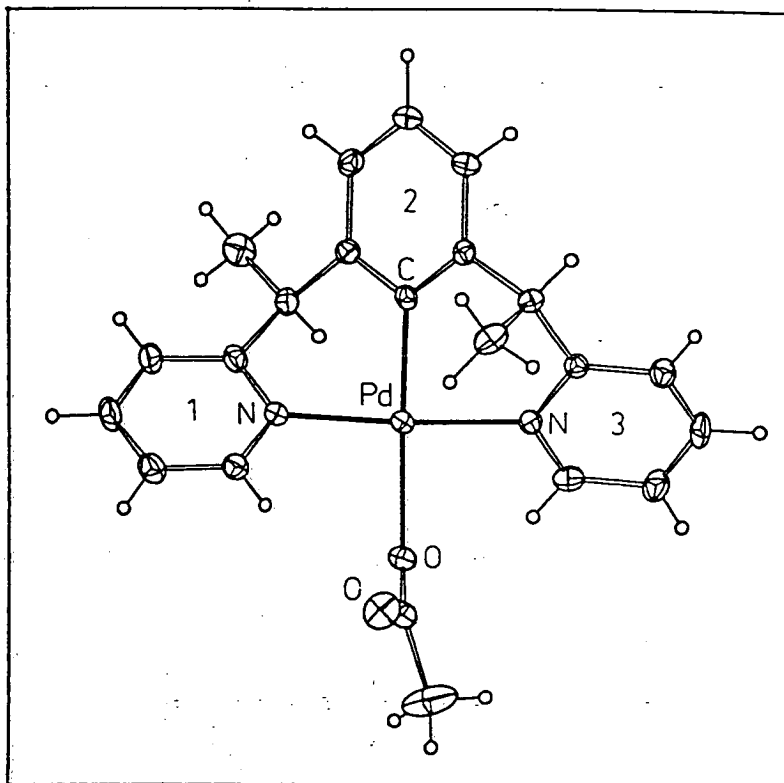
Distance (\AA)		Angle ($^\circ$)	
Pd - N(11)	2.050(5)	N(11) - Pd - C(21)	88.4(2)
Pd - C(21)	1.950(6)	C(21) - Pd - N(31)	88.5(2)
Pd - N(31)	2.036(5)	N(31) - Pd - O(1)	93.4(2)
Pd - O(1)	2.127(4)	O(1) - Pd - N(11)	89.7(2)

Dihedral Angle ($^\circ$) of rings to the plane ' N_2CO '.

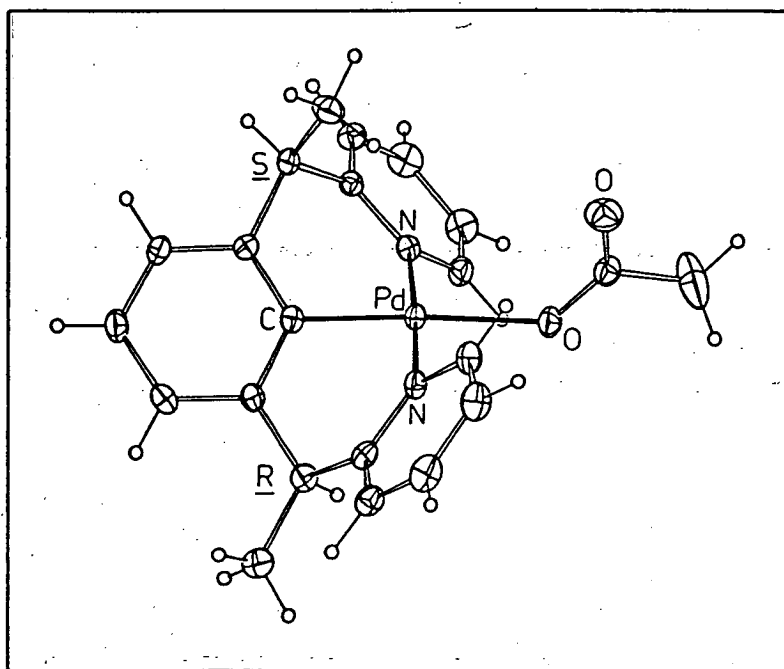
Ring	Angle
1	47.0
2	39.4
3	38.6



a) Viewed Normal to the 'N₂CO' Plane.

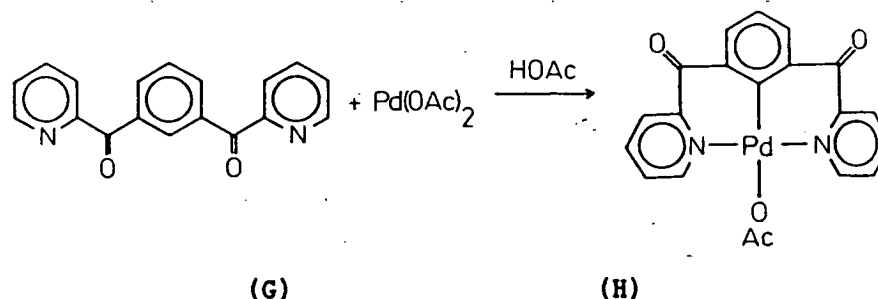


b) Viewed Normal to Ring 2.



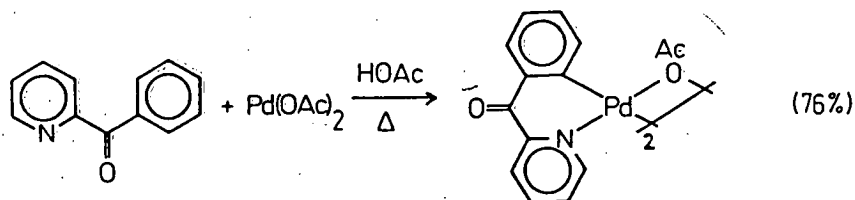
3.3(iv) Cyclometallation of an Extended Ketone.

Reaction of the benzene linked diketone (G), below, with $\text{Pd}(\text{OAc})_2$ in acetic acid (100°C , 4h) generated the metallation product (H) in good yield (72%).



The monomeric nature of product (H) has been established by osmometric molecular weight determination (found 445, calc. 454). Infrared absorptions for the acetato- group at 1616 cm^{-1} and 1374 cm^{-1} are indicative of unidentate coordination ($\Delta = 242\text{ cm}^{-1}$) and the carbonyl stretching frequency (1660 cm^{-1}) is similar to that observed for the free ligand (1668 cm^{-1}).

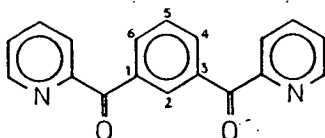
The product has some similarity to the previously reported dinuclear species shown below²³, generated in a similar manner from 2-benzoylpyridine and $\text{Pd}(\text{OAc})_2$.



In this complex the acetato- absorptions occur at 1584 cm^{-1} and 1430 cm^{-1} , indicative of bridging groups ($\Delta = 155\text{ cm}^{-1}$), and the carbonyl frequency occurs at 1670 cm^{-1} for both the complex and free ligand.

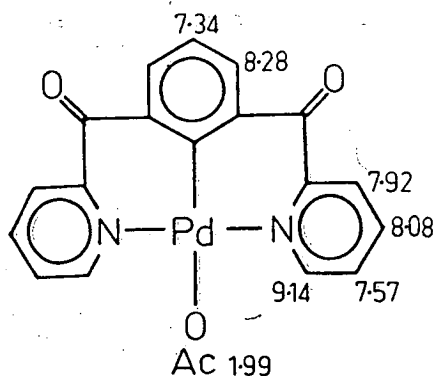
It is noteworthy that 2-benzoylpyridine, which contains an electron attracting carbonyl group, undergoes facile cyclometallation, in contrast with the results of earlier studies concerning the electronic effects on the cyclopalladation reaction of substituted azobenzenes.^{24,25} It is more surprising that in the presence of two mutually meta carbonyl groups

metallation occurs in the position indicated in (H). Carbonyl functionality deactivates the benzene nucleus towards electrophilic attack, and thus, in the diketone (G) position 2 on the benzene nucleus should be strongly disfavoured as a site for such attack.



In the formation of (H) it appears that two donors (N and/or O), separated by the benzene ring, may be actively involved in directing palladation.

The ^1H nmr spectrum of (H) may be fully assigned by examination of the standard spectrum as all proton environments are separated. Examination of splitting patterns and coupling constant information yields the following assignments,



3.3(v) The Solid State Structure of $[(\text{pyOC})_2\text{C}_6\text{H}_3]\text{Pd}(\text{OAc})$, Complex (H)

Crystals of the title complex were obtained by dissolution of a sample in dichloromethane/acetone (1:1) and diffusion of diethyl ether vapour in a sealed chamber.

The crystals are composed of two discrete conformers of the title complex in 1:1 ratio. Both molecules possess palladium in a square-planar coordination environment with the ligand present as an anionic planar-tridentate (N,C,N). The two molecules are shown

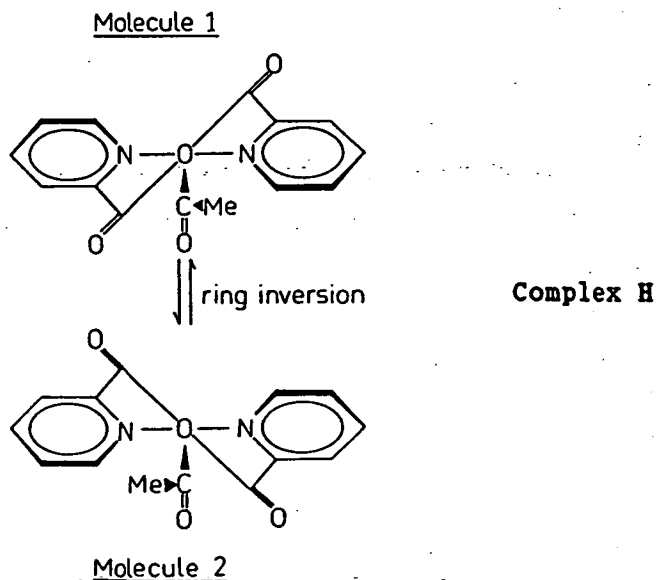
overleaf, with aspects of the geometry of both molecules given in Table 3.2. A view normal to the central phenyl ring (2) is shown on page 80, and this may be compared directly with *meso*- $[(\text{pyMeHC})_2\text{C}_6\text{H}_3]\text{Pd}(\text{OAc}) \cdot 1.5\text{H}_2\text{O}$, shown on page 75 (diagram (b)).

All aromatic rings in *molecule 1* are essentially planar with the greatest deviation from the mean planes, 0.03\AA , observed for C(33). In *molecule 2* the greatest deviation is observed for C(26), 0.28\AA .

For both molecules palladium is close to, or within, the projected mean plane of the phenyl ring, and the maximum deviation from other ring planes is 0.35\AA for ring 1 in *molecule 1*, and 0.25\AA from rings 1 and 3 of *molecule 2*. The dihedral angles subtended between the aromatic rings and ' PdN_2CO ' range from 32.7° to 42.5° (both in *molecule 2*).

The bond angles about the palladium atoms in *molecule 1* and *2* range from $88.6(3)$ to $91.3(4)^\circ$ with the tridentate ligand subtending angles C-Pd-N in the range $89.2(4)$ - $91.3(4)^\circ$. The angles defined by C-C-Z (Z = C, O, N, Pd), and C-N-Pd, range from $116(1)$ to $125(1)^\circ$, although most are approximately 120° .

Molecule 1 may be considered to be related to *molecule 2* by ring inversion analogous to that described for the *meso* isomer of complex (D) (page 69) in solution. Although ring inversion in (H) has not been observed using ^1H nmr spectroscopy (to -50°C), the solid state structure of (H) gives a clear illustration of the proposed effect.



$[(\text{pyOC})_2\text{C}_6\text{H}_3]\text{Pd}(\text{OAc})$ viewed Normal to the plane 'PdN₂CO'.

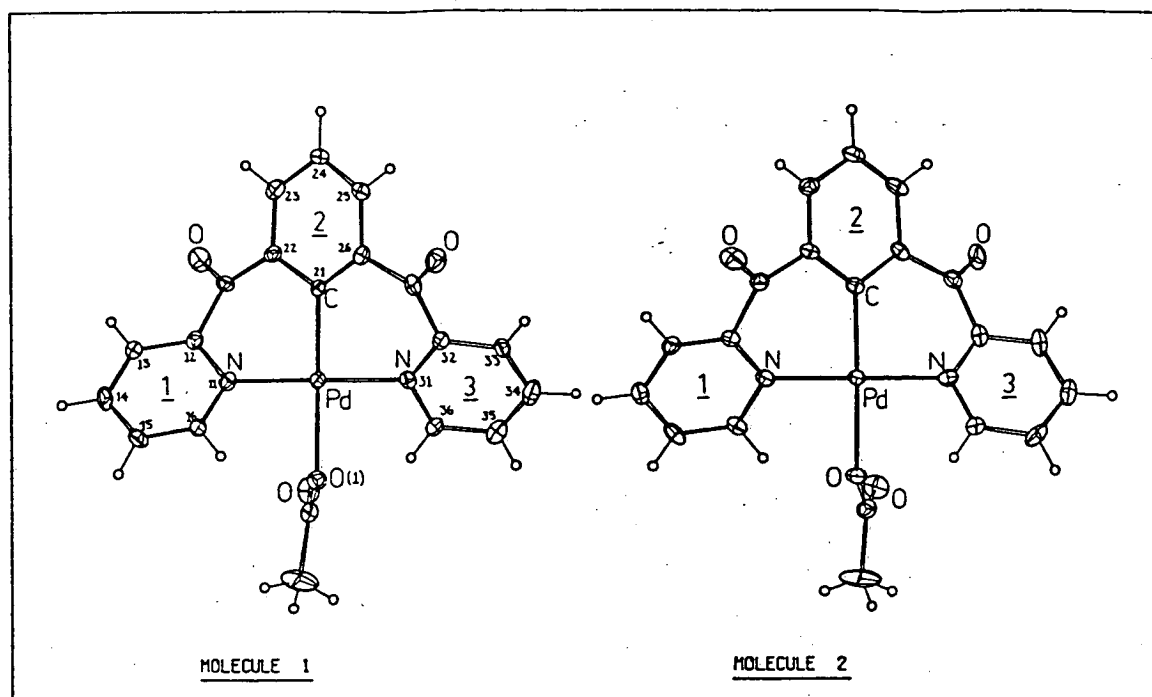


Table 3.2

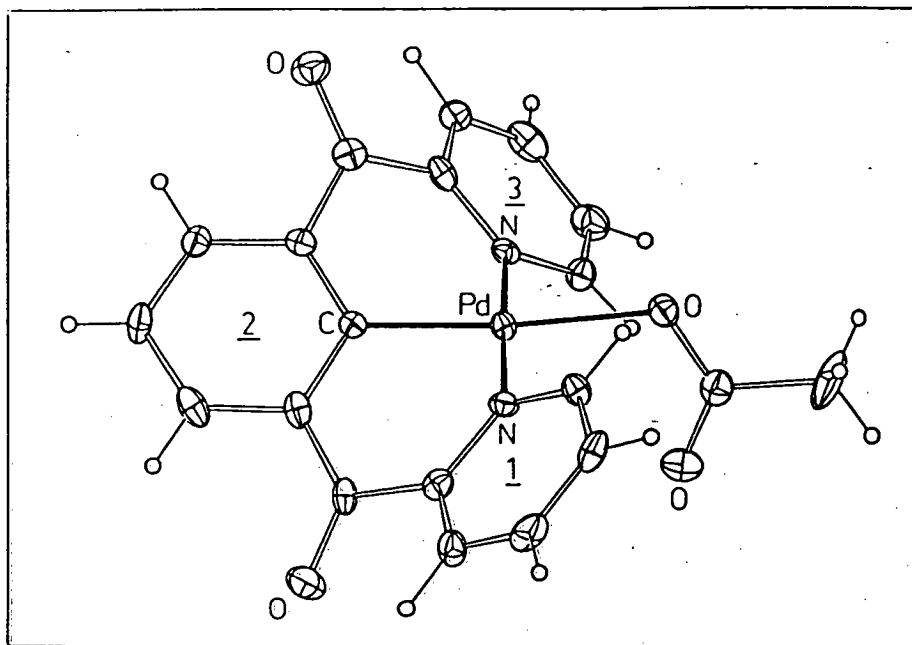
Palladium Environments

Distance(Å)/Angle(°)	Molecule 1	Molecule 2
Pd-N(11)	2.033(9)	2.030(10)
Pd-C(21)	1.963(11)	1.964(11)
Pd-N(31)	2.031(9)	2.027(10)
Pd-O(1)	2.137(8)	2.090(8)
N(11)-Pd-C(21)	91.3(4)	89.2(4)
C(21)-Pd-N(31)	89.7(4)	91.1(4)
N(31)-Pd-O(1)	90.5(3)	90.2(4)
O(1)-Pd-N(11)	88.6(3)	89.5(4)

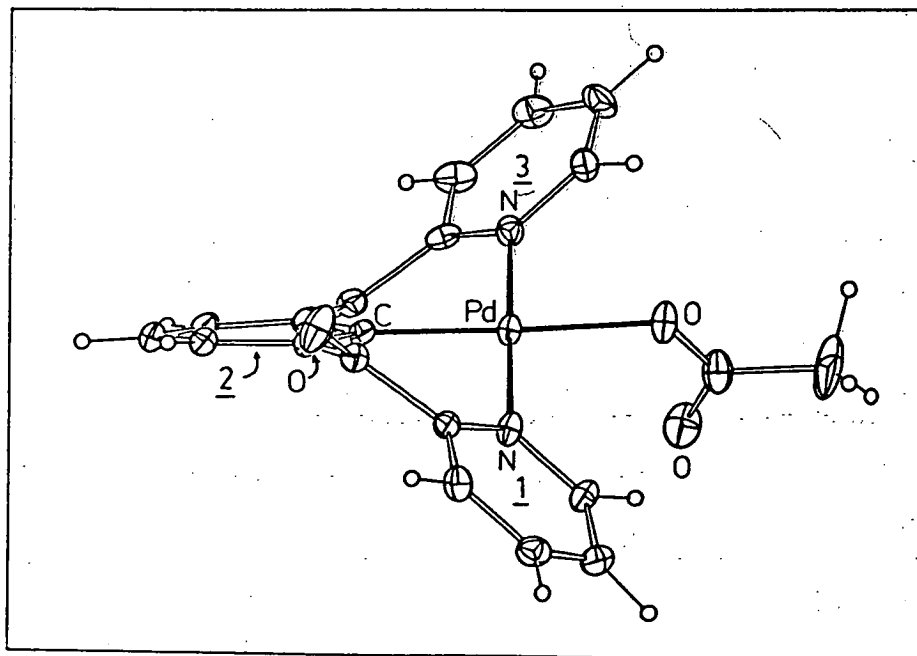
Dihedral Angles (°) of rings to the mean square plane 'PdN₂CO'.

Ring		
1	33.9	37.2
2	35.5	33.7
3	42.5	32.7

Alternative Views of Molecule 1 and 2 of $[(\text{pyOC})_2\text{C}_6\text{H}_3]\text{Pd}(\text{OAc})]$



Molecule 1 (viewed Normal to Ring 2)



Molecule 2

3.4 Conclusions

Metallation of simple ligands using $\text{Pd}(\text{OAc})_2$ in glacial acetic acid at or near reflux ($100-118^\circ\text{C}$) is only observed for the monodentate donor pyPh_2CH and produces an acetato-bridged dinuclear complex. In the presence of two or more adjacent donor groups only *N,N*-chelate complexes have been isolated and products containing $\text{Pd-C}(2)(\text{phenyl})$ or $\text{Pd-C}(3)(\text{pyridyl})$ groups, similar to the metallation products of 2-benzylpyridine with $\text{Pd}(\text{OAc})_2$, or 2,2'-bpy with $\text{Ir}(\text{III})$ or $\text{Pt}(\text{II})$, respectively, have not been detected.

For the extended ligands metallation has been observed to occur when pyridine donors are separated by a central 1,3-disubstituted benzene nucleus. In this instance exclusive metallation at the 2-position of the benzene ring produces monomeric palladated complexes, even in the presence of electron withdrawing carbonyl groups. These observations suggest that donors separated by the benzene ring interact with the metal and direct palladation.

In general, for both ligand types, palladation under the conditions stated only occurs when normal bi- or tridentate N-donor coordination of the ligand is not possible.

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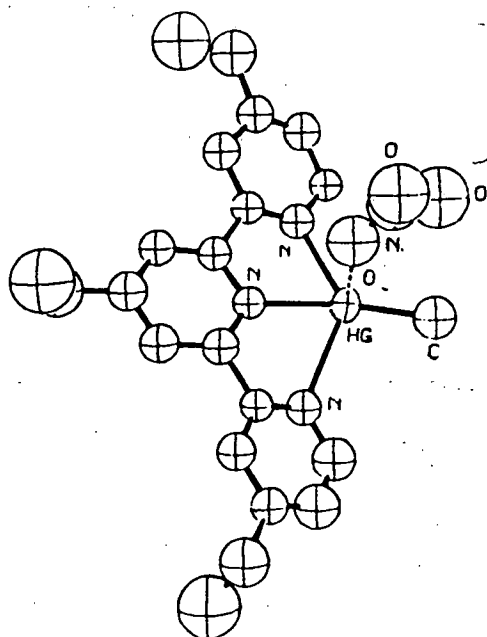
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CHAPTER FOUR

DIASTEREOISOMER SEPARATION USING METHYLMERCURY(II) NITRATE SALTS*4.1 Introduction

With polydentate nitrogen donor ligands methylmercury(II) readily adopts coordination geometries higher than the characteristic linear geometry observed for unidentate ligands¹⁻⁴. The higher coordination geometries are characterised by the presence of one Hg-N interaction stronger than the other(s), with the more strongly bound nitrogen forming the largest C-Hg-N angle, for example, in the complex of bis(pyridin-2-yl)methane the shortest Hg-N bond forms an angle C-Hg-N 172(1)^o, and the longest 106(1)^o.¹

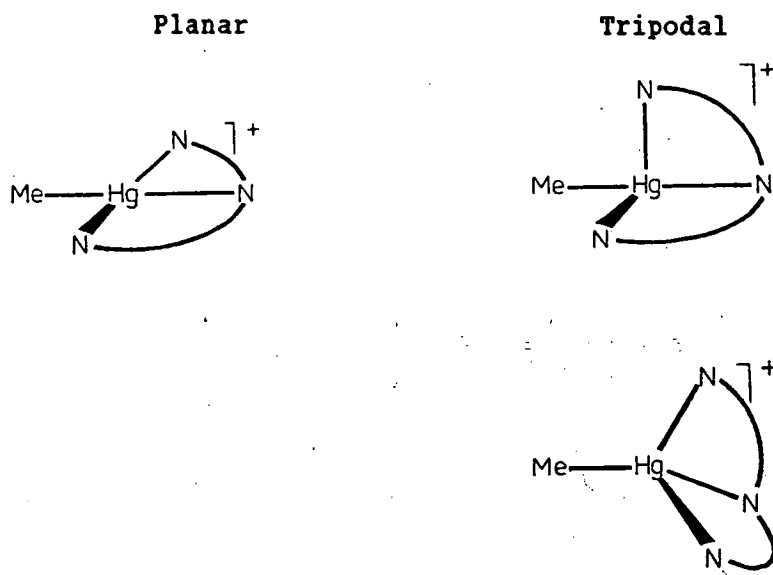
Although the complexes commonly have irregular geometries for polydentates, two of the tridentate ligands studied have a much smaller range of Hg-N distance and more regular geometries. Thus, the 4,4',4''-triethyl-2,2':6',2''-terpyridyl (Et₃tpy) complex¹ has distorted square-planar geometry with Hg-N 2.26(2)-2.61(2)Å (below), and the tris(pyridin-2-yl)methanol (py₃COH)² complex has distorted tetrahedral geometry with Hg-N 2.28(1)-2.53(1)Å and with C-Hg-N 119(1)^o (shown on page 14).

[(Et₃tpy)HgMe]NO₃

* Some material concerning this topic appears in Publication 3 page 224.

As both of these complexes involve pyridine donor groups, further investigation of these geometric effects have been sought via reaction of the tridentate 2,6-bis[1-phenyl-1-(pyridin-2-yl)ethyl]pyridine, $(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$, with methylmercury(II) nitrate.

The ligand has two chiral centers, and molecular models suggest that the *meso* and *racemic* diastereoisomers should both be able to act as planar-tridentates (similar to Et_3tpy), or tripodal-tridentates (similar to py_3COH), toward methylmercury(II), for example,



The *meso* form of the ligand has been shown to act as a planar-tridentate to $\text{Pd}(\text{OAc})_2$ (see page 30), allowing regular square-planar geometry to be achieved with 'trans' pyridine rings possessing an N-Pd-N angle of $177.8(2)^\circ$. The presence of a bridging carbon atom allows for a more regular square-planar geometry in comparison with, for example, $[(\text{tpy})\text{PdCl}]^+$ where 'trans' pyridine rings possess an N-Pd-N angle of 161° .⁵

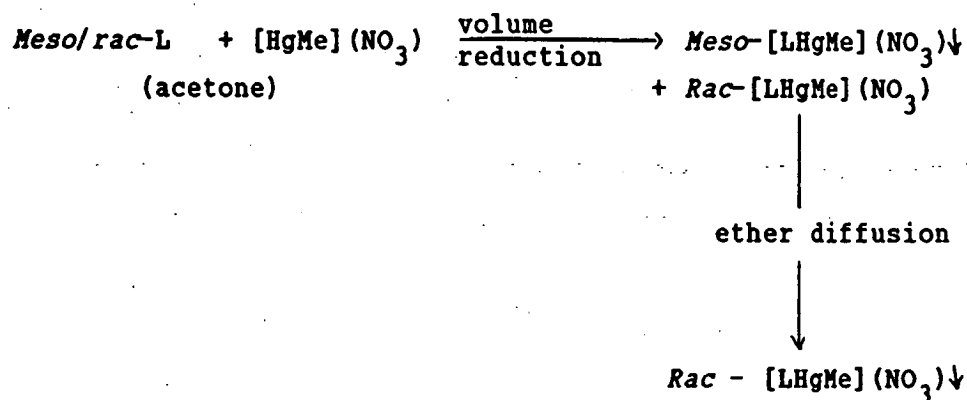
4.2 Synthesis and Characterisation of *Meso*-/*Rac*-(pyPhMeC)₂C₅H₃N₂L, and *Meso*- and *Rac*-[LHgMe](NO₃) Complexes

The synthetic route devised for the preparation of the ligand is shown on page 165 and experimental details are given on pages 211 and 212.

The ligand, composed of *meso*-L and *rac*-L, gives a ¹H nmr spectrum that does not clearly indicate the differences between the diastereoisomers in contrast to, for example, the spectrum of *meso/rac*-(pyPhHC)₂ shown on page 99. Thus, the proportions of diastereoisomers cannot be determined by these means. After five developments on analytical silica gel plates with chloroform solvent, two maxima are observed using U.V. and iodine stain detection in an extended spot (*R_f* 0.83-0.65).

Protonation constants of the unseparated ligand in dioxane-water (1:1) were measured using an automated equilibrium titrator with microcomputer implementations of MINQUAD 75.^{6,7} Potentiometric titration data were satisfactorily treated as arising from successive protonations of the ligand with log *K_H* for the equilibria calculated as 3.87 and 2.28 for successive protonations.

The complexes *meso*- and *rac*-[LHgMe](NO₃) were prepared by dissolution and combination of the unseparated ligand and methylmercury(II) nitrate in acetone solution, followed by slow evaporation of solvent, then ether diffusion in a sealed chamber.



The complexes have satisfactory microanalyses and ¹H nmr spectra indicating L:MeHg, 1:1. Both complexes are hydrates, and as the *meso*-L complex has been shown to be dihydrate from

crystallographic studies, the *rac*-L complex is formulated similarly in view of the unreliability of microanalytical values in estimating the extent of hydration. The complexes exhibit identical ^1H nmr spectra, but slightly different I.R. spectra in the region $1100\text{--}500\text{ cm}^{-1}$.

4.3 Solid State Structure of *Meso*-[LHgMe](NO₃).2H₂O⁸

Aspects of the geometry of *meso*-[LHgMe]⁺ and the nitrate ion are given in Table 4.1. The cation structure is shown overleaf and may be compared with that of *meso*-[LPd(OAc)]⁺ on page 30. Neighbouring cations are related by inversion centres, with atoms C(7) and C(9) having chirality *S* and *R*, respectively. The nitrate ion is regular (within 2σ in bond lengths and angles) and is uncoordinated.

Meso-L is present as a tripodal tridentate, with N-Hg-N angles $76.0(3)^\circ$ (rings A, B), $88.3(3)^\circ$ (A,C), and $75.3(3)^\circ$ (B,C). The central ring (B) is more strongly bound to mercury, with Hg-N(B1) [$2.283(9)\text{\AA}$] shorter than Hg-N(A1) [$2.546(11)\text{\AA}$] and Hg-N(C1) [$2.595(10)\text{\AA}$]. The mercury-nitrogen bond lengths differ by only $0.02\text{--}0.05\text{\AA}$ from those of both tripodal py_3COH and Et_3tpy , although the Et_3tpy complex has the mercury atom well removed from the mean planes of the (outer) weakly coordinated rings (-0.886\AA , -1.032\AA) compared with -0.46\AA (ring A) and -0.25\AA (ring C). The central nitrogen has C-Hg-N(B1) $166.3(5)^\circ$, intermediate between that for the py_3COH complex [$150(1)^\circ$] and Et_3tpy complex [$171(1)^\circ$].

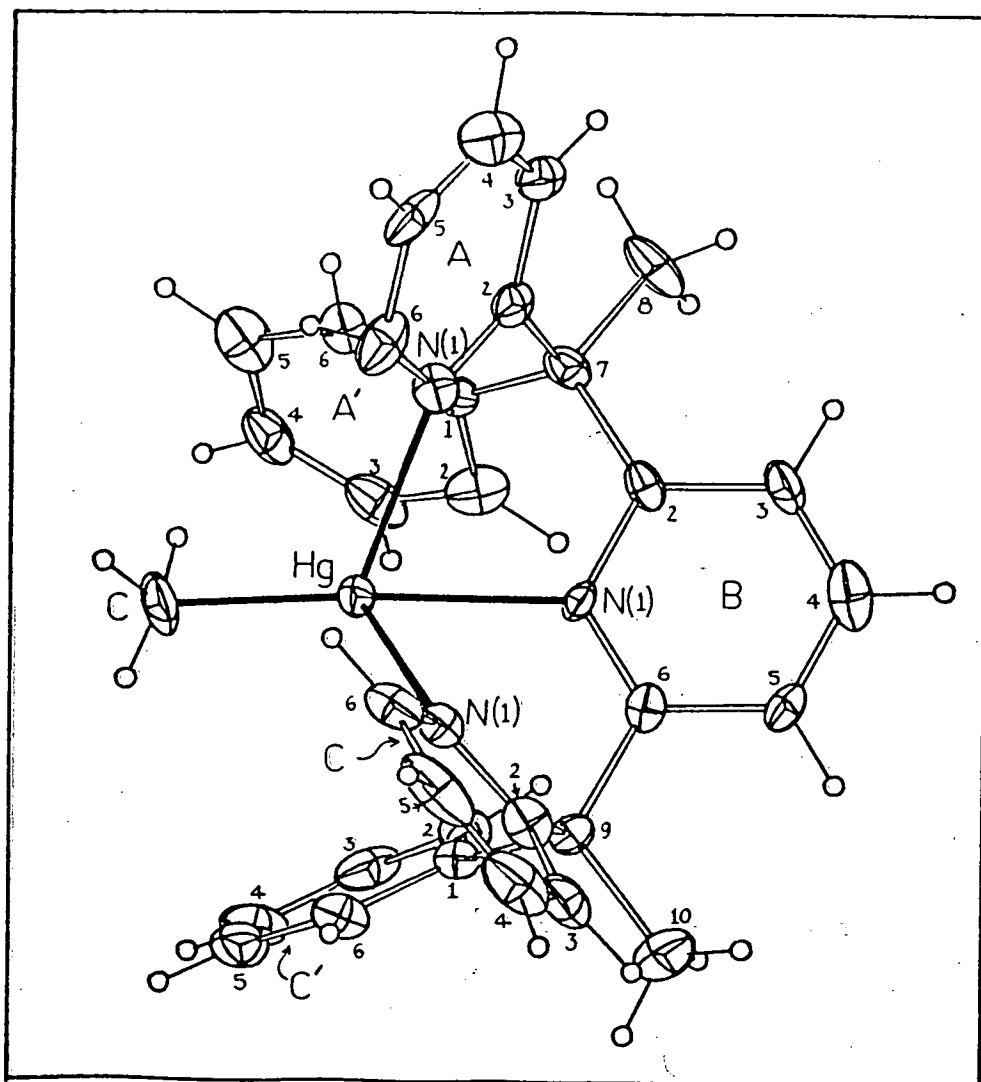


Table 4.1

Coordination geometry for the mercury atom and nitrate ion in
Meso-[LHgMe]N₃·2H₂O; distances in Å, angles in degrees.

Hg-N (A1)	2.546(11)	Hg-N(C1)	2.595(10)
Hg-N (B1)	2.283(9)	Hg-C	2.048(15)
N(A1)-Hg-N(B1)	76.0(3)	Hg-N(A1)-C(A2)	118.4(8)
N(C1)-Hg-N(C1)	88.8(3)	Hg-N(A1)-C(A6)	122.5(9)
N(B1)-Hg-N(C1)	75.3(3)	Hg-N(B1)-C(B2)	118.3(7)
N(A1)-Hg-C	113.3(5)	Hg-N(B1)-C(A6)	120.2(8)
N(B1)-Hg-C	166.3(5)	Hg-N(C1)-C(C2)	115.5(7)
N(C1)-Hg-C	113.7(5)	Hg-N(C1)-C(A6)	123.0(9)

Deviation of the Hg from the 'C₅N' mean planes of rings A,B,C:
 -0.46, 0.46, -0.25 Å.

Nitrate ion: N-O(1,2,3) 1.06(3), 1.11(3), 1.16(3) Å
 O(1)-N-O(2,3) 117(2), 121(2); O(2)-N-O(3), 120(2)°.

4.4 Structure of the Complexes in Methanol and Isolation of *meso*- and *rac*-L.

As the *meso* complex has two mercury-nitrogen interactions much weaker than the central pyridine interaction, it is possible that the complexes may have a different structure(s) in solution involving a lower coordination number(s), for example, Et_3tpy is a tridentate in the solid state but bidentate in methanol.¹

For pyridine and fourteen substituted pyridines, including some with substituents in the 2- and 6- positions, for example, 2,6-dimethylpyridine and the bulky $-\text{CHPh}_2$ group in α -phenyl- α -(pyridin-2-yl)toluene, the relationship

$$^2J(^1\text{H} - ^{199}\text{Hg}) = -2.96 \log K_{\text{H}} + 241.6 \text{ Hz}$$

has been established,⁶ where $\log K_{\text{H}}$ is the apparent protonation constant of the ligand determined in 50% dioxane-water. For polydentate pyridine donors, the coupling constant is higher than expected from this relationship if the ligand is coordinating as a bidentate or tridentate.^{1,2,9} For *meso*- $[\text{LHgMe}]^+$ and *rac*- $[\text{LHgMe}]^+$ the coupling constant is ca. 25 Hz greater than expected for unidentate binding, involving the same nitrogen as occurs on protonation, and thus the complex(es) in solution involve polydentate coordination.

The chemical shift of the $\text{Hg}^{\text{II}}\text{Me}$ protons, -0.35 ppm, is further upfield than observed for any other complex ion $[\text{LHgMe}]^+$, where L is a pyridine donor (0.70-1.16 ppm),^{1,2,9,10} consistent with presence of two phenyl groups in orientations resulting in anisotropic shielding of the methyl protons, for example, as observed on comparison of spectra for L=pyridine (1.08 ppm) and 2-benzylpyridine (0.79 ppm).⁹

The ligand is very insoluble in water, and thus the *meso* and *racemic* diastereoisomers were readily isolated from their complexes in high yield (86 and 97%, respectively), by formation of water soluble methylmercury-cyanide. Methylmercury cyanide has $\log K$ 14.1 in water,¹¹ considerably higher than that expected for the complexes, for example, $[(\text{tpy})\text{HgMe}]^+$ has $\log K$ 6.35 in water.¹²



The diastereoisomers have identical mass spectra to that of L, but slightly different melting point, I.R. spectra in the region 900-500 cm^{-1} , and ^1H nmr spectra in the region 7.6 - 6.9 ppm. The *meso* diastereoisomer has M.Pt. 101-101.5°; *rac*-L, 98-99.5°; and a ca. 1:1 mixture of *meso*- and *rac*-L, 95-96°. The *meso* and *racemic* forms have slightly different R_f values, *meso*-L, 0.80-0.68; *rac*-L, 0.78-0.65, and the unseparated ligand 0.83-0.65, after five developments in chloroform on analytical silica gel plates. The separated diastereoisomers have subsequently been used in preparation of complexes of $\text{Pd}(\text{OAc})_2$ (see pages 39 and 44).

4.5 Conclusions

The flexibility in coordination behaviour of the *meso* form of the ligand, the synthesis of the diastereoisomer mixture (L) in moderate yield (ca. 30%) from 2-benzylpyridine, and the straightforward separation of *meso*-L and *rac*-L from their $[LHgMe]^+$ complexes, indicate that the new ligand may be of value to studies in coordination chemistry generally, for example, as a pyridine analogue of tridentate diethylenetriamine, and as a relative of planar 2,2':6',2"-terpyridyl and tripodal tris(pyridin-2-yl)methane.

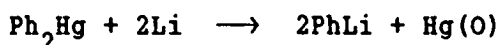
* ~~It has been found that addition of a few drops of acetone to the suspended complex in cyanide solution reduces surface tension and allows the reaction to proceed more rapidly.~~

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CHAPTER 5

THE INTERACTION OF SIMPLE LIGAND ANIONS WITH MERCURIC IODIDE*5.1 Introduction

One traditional application of organomercurials in synthesis has utilised their ability to transfer organic groups to other metals to prepare new organometallic compounds. Thus, the reaction of diorganomercurials with metals of groups I, II, and III is one of the classical routes to organometallic compounds, for example, to "salt-free" lithium reagents.¹

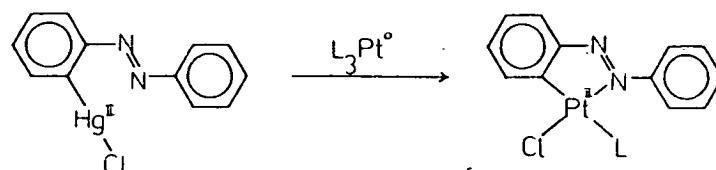


More recently, the capacity of organomercurials to transfer organic groups to Ni(0), and Pt(0) has been recognised,² and similar reactions have also been noted for these metals in oxidation state (II).³ The reaction between organomercurials and Pt(0) complexes has provided an efficient route to, for example, σ -organoplatinum(II) compounds including aryl, vinyl, heteroaryl, and alkyl derivatives.² A frequent advantage of this reaction is that the transferable group may contain functional substituents incompatible with Grignard or organolithium reagents. The approach has also generated examples of complexes containing stable platinum-mercury σ -bonds, and allowed related bimetallic intermediates of a similar nature to be isolated.⁴

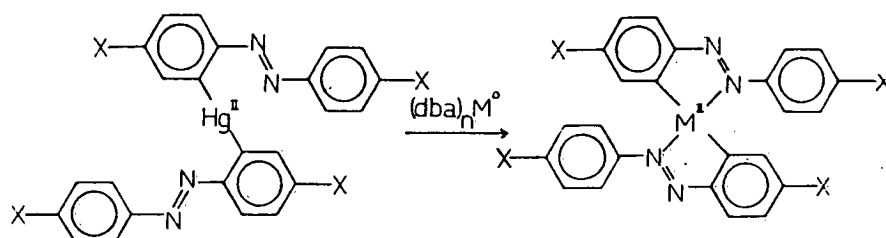
The addition of organomercurial to Pd(0) and Pt(0) complexes is facilitated by use of the ancillary ligand dibenzylideneacetone, (dba)^{5,6}. The complexes (dba)_nPd(0) and (dba)_nPt(0) (n=2 or 1.5+0.5(solvent)) are readily obtained and are stable in the solid state. As a ligand, dba is only retained by the metal in the zerovalent state, and thus, in the presence of, for example, an N-donor group in the organomercurial, C,N-donor complexes may form with displacement of Hg(0). The

* Published material concerning this topic appears in Publications 1 and 6, pages 220, and 240, respectively.

advantage of dba complexes over phosphine containing complexes results from facile ancillary ligand displacement. Complete removal of phosphines from products is difficult and not always possible.

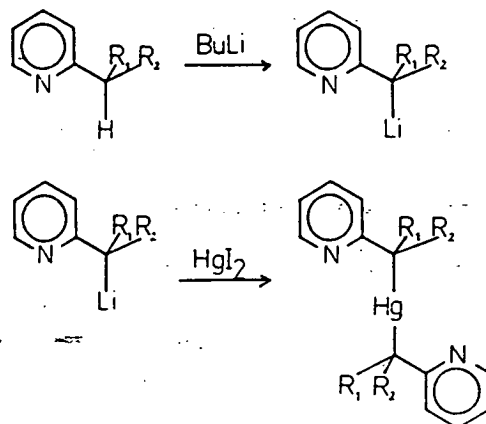


L=tertiary phosphine
(Ref. 7)



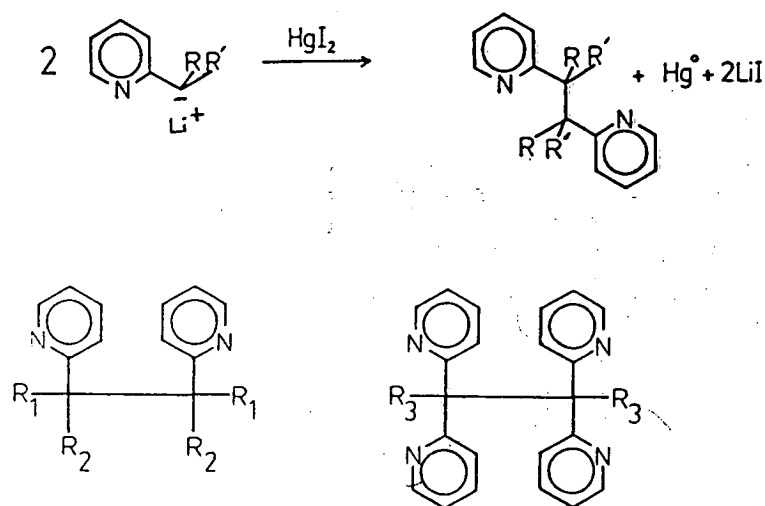
(Ref. 8)

Thus, for investigation of the synthesis of organopalladium(II) complexes involving the proposed formation of Pd-C(alkyl) bonds, diorganomercurial reagents of the form $[(pyR_1R_2C)_2Hg]$ (where $R_1, R_2 = H, Me, Ph, \text{ or } py$) have been sought using the method below.



5.2 Synthesis of Poly(pyridin-2-yl)ethanes and Related Dimers

In attempting to perform the reaction sequence illustrated above, $\text{pyR}_1\text{R}_2\text{C}^-\text{Li}^+$, generated from lithium-hydrogen exchange of the ligand in tetrahydrofuran (THF) with butyllithium (hexane solution), was reacted with HgI_2 in THF in 2:1 mole ratio at ambient temperature.* On slow addition of THF solutions of HgI_2 to the lithiated ligands immediate precipitation of mercury was observed in all cases except for $\text{py}_2\text{CH}^-\text{Li}^+$, which precipitated mercury slowly at ambient temperature and more rapidly at reflux (ca. 66°C). Subsequent hydrolysis was followed by isolation of dimers $(\text{pyR}_1\text{R}_2\text{C})_2$ in 16-85% yield (see Experimental, pages 193 - 197). For 2-methyl- and 2-ethylpyridine tarry products were obtained and these were not studied further.



For comparison, diphenylmethane was also lithiated under similar conditions and reacted with HgI_2 giving the previously reported¹⁷ dimer 1,1,2,2-tetraphenylethane (16%), some reduced mercury, and di(n-butyl)mercury (^1H nmr, M.S. identification). In

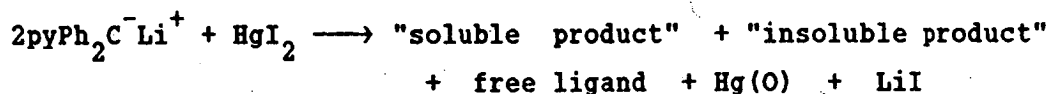
* For 2-benzylpyridine the reaction was also attempted at low temperature (-80°C), and in diethyl ether at ambient temperature and -80°C . Similar results to the above were obtained in all instances.

this instance the low yield of the dimer may be attributed, in part, to incomplete lithiation (for example, see ref. 16).

The dimers A and C, which have been reported earlier,¹⁰⁻¹⁵ were characterised by ^1H nmr, infrared, and mass spectra, melting point, and osmometric molecular weight determinations in chloroform at 37°C . The new compounds, B, D, and E, were characterised similarly, together with microanalysis.

Reaction under similar conditions of lithiated triarylmethanes of the general form $\text{py}_n\text{Ph}_{3-n}\text{C}^-\text{Li}^+$ ($n=0-3$) with HgI_2 resulted in isolation of rather insoluble organic products for $n = 1-3$, presumably of a polymeric nature. For $n = 0$, Ph_3C^- , the known compound triphenylmethylperoxide¹⁸ was obtained (68%, ^1H nmr, M.S., I.R. identification), suggesting triphenylmethyl radicals were present in solution prior to workup (O_2 present).

For $n = 1$, pyPh_2C^- , two organic products were obtained. Both exhibited nearly identical ^1H nmr and I.R. spectral characteristics although one was considerably more soluble in organic solvents than the other, and differences in crystallinity and melting point were evident.



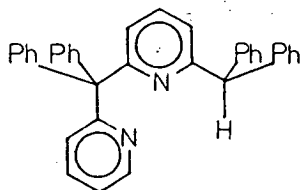
The "insoluble product", isolated as an amorphous white powder, analysed for $(\text{C}_{18}\text{H}_{14}\text{N}_1)_n$, similar to the free ligand $(\text{C}_{18}\text{H}_{15}\text{N}_1)$. The mass spectrum showed a parent ion at 488 m.u. (i.e. dimer) but molecular weight determinations in chloroform showed concentration dependence with dilute solution ($\text{ca. } 2 \times 10^{-3} \text{ M}$ in CHCl_3) indicating a molecular mass of $\text{ca. } 1,300$.

The "soluble product" was readily recrystallisable from dichloromethane/acetone giving colourless crystals, but microanalytical figures from two preparations indicated the presence of an element other than C, H, or N (found; C 86.7%, H 5.8%, N 5.5%, calc. for dimer; C 88.5%, H 5.8%, N 5.7%). The mass spectrum showed a parent ion at 488 m.u. (i.e. dimer) and

osmometric molecular weight determination (ca. $3 \times 10^{-2} M$ in CHCl_3) indicated a molecular mass of ca. 520.

For both products ^1H nmr spectra show the presence of pyridine H(6) and methine environments, as well as complex overlapping resonances associated with pyridine H(3-5) and phenyl protons. The ^{13}C nmr (^1H -decoupled) spectra of free ligand, "soluble product", and "insoluble product", show respectively, 9, 18, and $\gg 30$ lines. Thus, the soluble product is tentatively formulated as a dimer, while the insoluble product is presumably a polymer.

The presence of methine proton signals in both products indicates that linkage between ligand units does not occur through both bridging carbon atoms, a feature shared by the triphenylmethane dimer, ¹⁹⁻²¹ and by some diarylmethanes.²² Comparison of the integration ratio for the soluble and insoluble products between H(6) and CH resonances suggests that the following type of linkage is present,

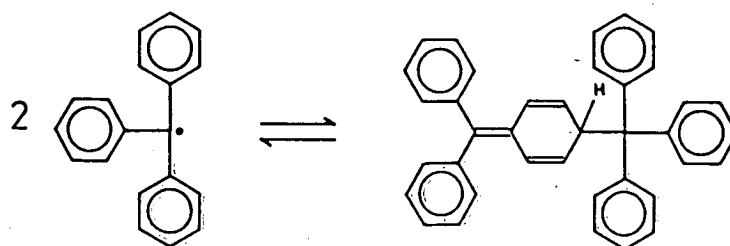


Similar reactions between $\text{py}_2\text{PhC}^-\text{Li}^+$ ($n=2$) and $\text{py}_3\text{C}^-\text{Li}^+$ ($n=3$) with HgI_2 yielded sparingly soluble amorphous powders, similar to the insoluble product described above. However, as both were contaminated with traces of HgI_2 (detected by M.S.) that could not be satisfactorily removed, further study of these products was not attempted.

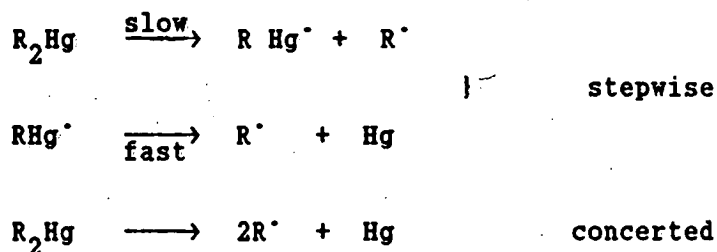
The dimers presumably form via transient dioganomercurials which decompose to mercury and coupling products. However, the intermediate(s) formed prior to dimerisation may be dependent on the individual ligand. For example, the dimer $(\text{py}_2\text{HC})_2$ is only formed readily at elevated temperature, preceded by formation of an orange solid, whereas the analogous dimer $(\text{pyPhHC})_2$ forms instantly, assuming precipitation of $\text{Hg}(0)$ is indicative of dimer formation. Isolation of the orange solid formed prior to isolation of $(\text{py}_2\text{HC})_2$ in a pure state was not possible due to

contamination by traces of Hg(0) and LiI. The solid darkens in a nitrogen atmosphere over a few hours.

Reaction of triarylmethyl anions containing a pyridin-2-yl substituent with HgI_2 apparently produces free radicals of a similar nature to the triphenylmethyl radical below. Dimerisation does not occur by linkage of bridging carbon atom presumably due to the steric constraint caused by the aromatic rings. Thus, condensation occurs between a bridging carbon atom and an aromatic ring.²²



Decomposition of diorganomercurials accompanied by free radical dimerisation is well known and has application in organic synthesis.²³ Such decomposition reactions may be sponsored by photochemical,²⁴ thermal,²⁵ and transition metal catalysed processes.^{26,27} Two classes of decomposition are recognised, stepwise and concerted.



Decomposition often gives a complex mixture of products, and frequently when photolysis or thermolysis is carried out in solution the products obtained include those originating from radical attack on the solvent. Although the products obtained in this study do not distinguish the likely decomposition mechanism(s), the high yields of the dimers $(\text{pyPhHC})_2$ and $(\text{py}_2\text{HC})_2$ (80% and 85%, respectively) indicate that extensive attack on solvent does not occur in these cases.

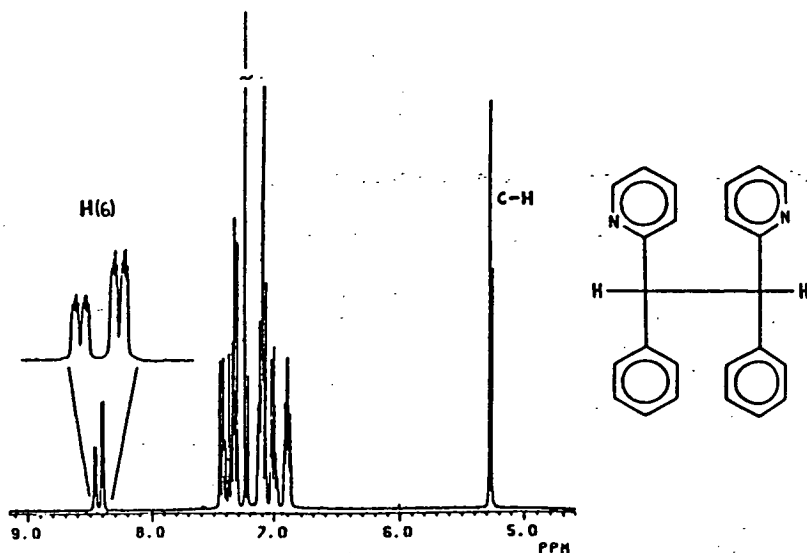
5.3 Characterisation of Poly(pyridin-2-yl)ethane Dimers and some Palladium(II) Acetate Derivatives

The poly(pyridin-2-yl)ethanes may be of general interest in coordination chemistry. For example, $(\text{pyPhHC})_2$ may act as a bidentate ligand forming a seven membered chelate ring as a heterocyclic analogue of *meso* and *racemic*-stilbenediamine, $[(\text{NH}_2)\text{PhHC}]_2$, which forms Lifschitz salts.²⁸

The dimers $(\text{pyRHC})_2$ ($\text{R}=\text{py}, \text{Ph}$) are produced in high yield from the corresponding monomers and may possibly act as bridging or bidentate ligands, forming either six- or seven-membered chelate rings. Thus, to investigate the coordination properties of $(\text{pyRHC})_2$ ($\text{R}=\text{Ph}, \text{py}$), complexes of palladium acetate were formed in a similar manner to those described on page 19.

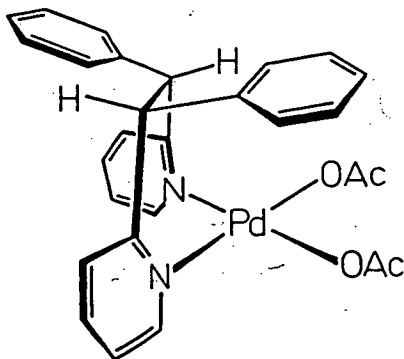
For $(\text{pyMe}_2\text{C})_2$ and $(\text{py}_2\text{RC})_2$ ($\text{R}=\text{H}, \text{Me}$) ^1H nmr spectra show one pyridine ring environment, the spectrum of $(\text{py}_2\text{HC})_2$ shows one methine environment, and both $(\text{pyMe}_2\text{C})_2$ and $(\text{py}_2\text{MeC})_2$ show one methyl environment.

The dimers $(\text{pyPhRC})_2$ ($\text{R}=\text{H}, \text{Me}$) are formed as mixtures of *meso* and *racemic* diastereoisomers. For $(\text{pyPhHC})_2$ complex pyridine H(3-5) and phenyl resonances are observed but with H(6) and corresponding methine resonances divided in ca. 3:2 ratio (see spectrum below). The dimer $(\text{pyPhMeC})_2$ exhibits two pyridine H(6) and H(4) resonances in ca. 3:1 ratio, but has unresolved methyl resonances.



Complexes of stoichiometry $[(\text{pyPhHC})_2\text{Pd}(\text{OAc})_2]$ and $[(\text{py}_2\text{HC})_2\{\text{Pd}(\text{OAc})_2\}_2]$ were readily obtained from benzene solution in 18% and 64% yield, respectively. Both complexes exhibit I.R. spectra appropriate for unidentate acetate coordination with $\Delta[\nu_{\text{as}}(\text{CO}_2^-) - \nu_{\text{s}}(\text{CO}_2^-)] > 200 \text{ cm}^{-1}$,²⁹ although the complex of $(\text{pyPhHC})_2$ appears to have more than one $\nu_{\text{s}}(\text{CO}_2^-)$ absorption. Thus, $\nu_{\text{as}}(\text{CO}_2^-)$ occurs at 1640 cm^{-1} with $\nu_{\text{s}}(\text{CO}_2^-)$ and/or $(\text{pyPhHC})_2$ absorption at 1382 ($\Delta = 258$), 1360 (280) and 1314 (326) cm^{-1} . The complex containing $(\text{py}_2\text{HC})_2$ has acetate absorptions at 1634 and 1312 ($\Delta = 322$) cm^{-1} .

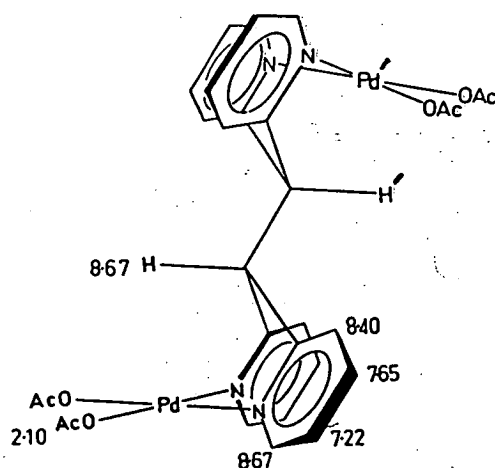
The dimer $(\text{pyPhHC})_2$, composed of both *meso*- and *racemic* diastereoisomers, gave a palladium acetate complex in low yield (18%), and the ^1H nmr spectrum of the complex is consistent with presence of the *racemic* diastereoisomer only. Thus, the two methine doublets (9.03 and 4.99 ppm, $J(\text{CHCH})$ 12.6 Hz) correspond to the presence of two methine environments with a large dihedral angle where decoupling experiments indicate that these resonances arise from protons within the same molecule.



The methine resonance with chemical shift furthest from that of the free ligand (9.03 ppm, shifted 3.75 or 3.77 ppm downfield) is assumed to result from the proton closest to palladium (see page 126). Consistent with this structure two pyridine and phenyl ring environments, for example, H(6) doublets at 9.68 and 8.86 ppm, Ph(*ortho*) doublets at 8.04 ppm and 7.86 ppm, and two acetate group environments (singlets at 2.06 and 1.97 ppm) are exhibited in the ^1H nmr spectrum, and acetate absorption in the I.R. spectrum is complex (see above). Molecular models suggest that the *racemic* form has lower intramolecular steric interactions than a complex of the *meso* form of the ligand.

A more complete proton assignment has been made using COSY spectroscopy and details are shown on page 104. Assignment by examination of coupling constants has not been possible due to the complexity of the resonance patterns.

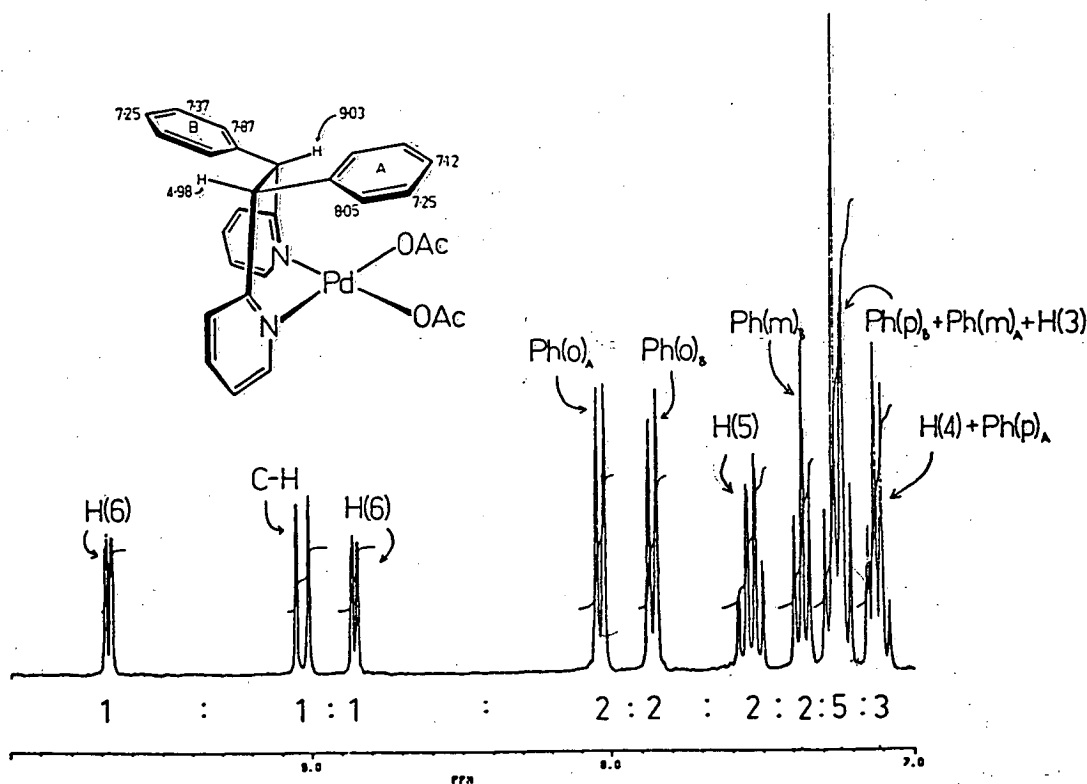
For the complex containing $(py_2HC)_2$, acetate absorption in the I.R. (see above) and the 1H nmr spectrum are much simpler. Microanalysis and the presence of a single methine and acetate resonance are consistent with the ligand bridging two $Pd(OAc)_2$ moieties forming six-membered chelate rings, as molecular models suggest that seven-membered chelate rings would have a conformation similar to that of the *rac*-(*pyPhHC*)₂ complex, resulting in two acetate and aromatic ring environments. The simplicity of the 1H nmr spectrum allows full proton assignment from examination of coupling constant information.



Although it has been found, in general, that sterically demanding groups on a bridging carbon atom are placed axially over the metal atom the converse has been assumed for this complex. The large downfield shift of the methine proton resonance (8.67 ppm) compared with that of the free ligand (5.74 ppm) suggests close proximity to a metal center (see page 126). Molecular models indicate that placement of the bulky group over the metal atom would demand very close contact between Pd and H', and Pd' and H.

5.3(i) The COSY Spectrum of *Rac*-[(pyPhHC)₂]Pd(OAc)₂

To improve aromatic proton assignment a COSY spectrum of the title complex was obtained. Using the readily identified pyridine H(6) and phenyl(ortho) proton resonances in the standard ¹H nmr spectrum the resonance position of H(5) and phenyl(meta) protons could be firmly established. However, resonance overlap as well as weak J-coupling preclude definite assignment of pyridine H(3) and H(4), as well as phenyl(para) protons. The following assignments have been made in conjunction with integration ratios.



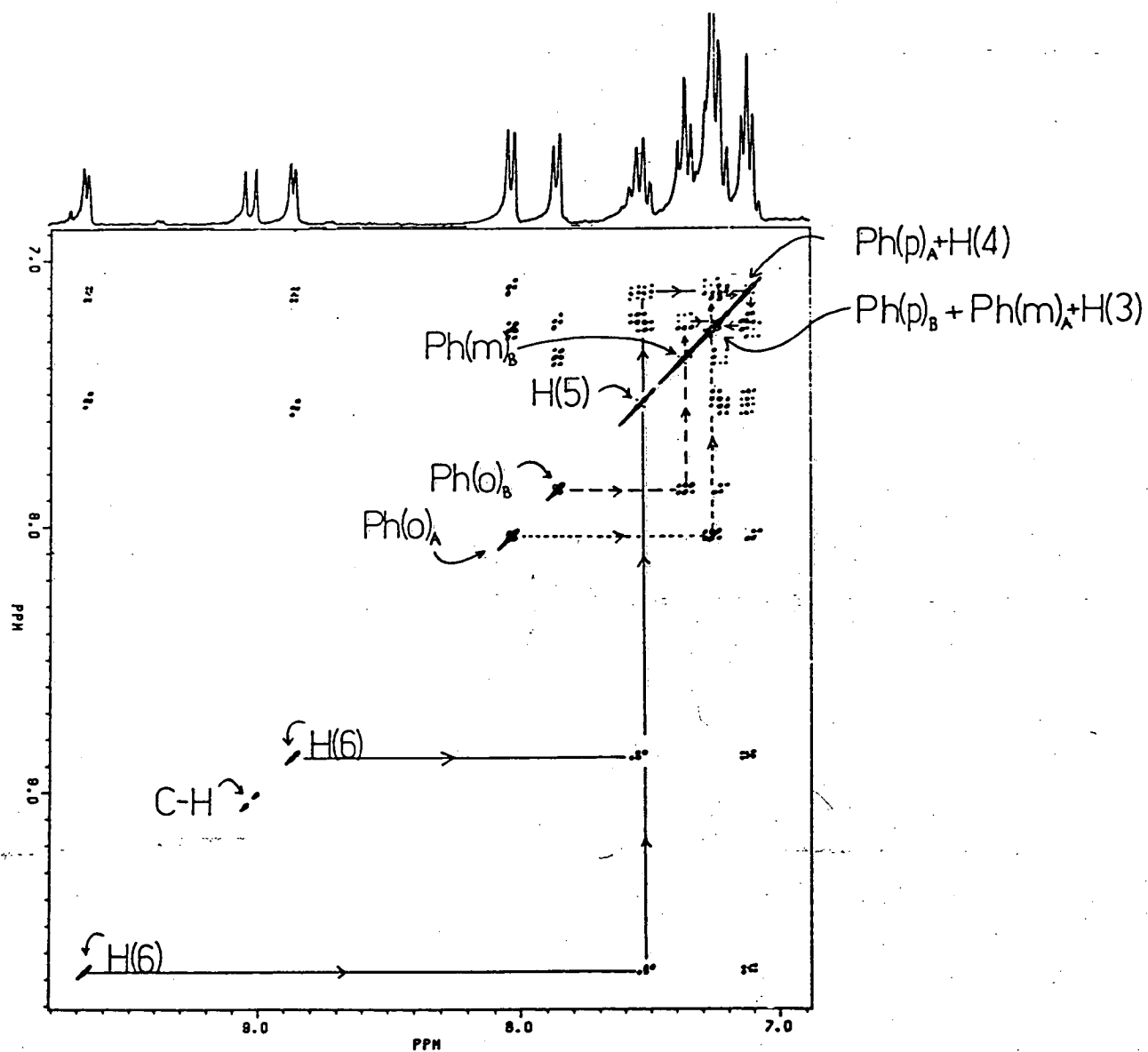
The indistinguishability of H(3-5) resonances in the two pyridine ring resonances, in comparison with the large chemical shift difference observed between H(6) environments, is presumably a result of the H(3-5) environments being remote from the metal center.

5.4 Conclusions

Attempts to form the reagents [(pyR₁R₂C)₂Hg] have not been successful, resulting instead in a convenient synthesis of dimers of the form (pyR₁R₂C)₂. These may be useful ligands in their own

right. Reaction of two dimers with $\text{Pd}(\text{OAc})_2$ indicate that the ligands may chelate to form six- or seven-membered rings, and that diastereoisomer selectivity in crystallisation occurs in one instance.

The COSY Spectrum of $\text{Rac-}[(\text{pyPhCH})_2\text{Pd}(\text{OAc})_2]$
(Aromatic Region)

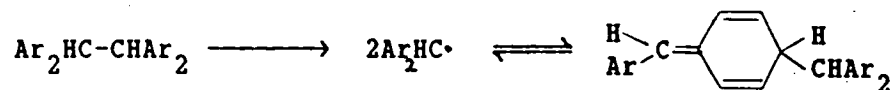
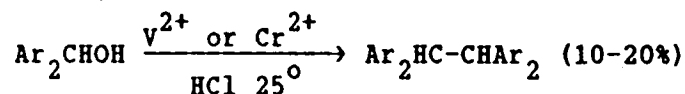


- Connectivity in Ring A.
- Connectivity in Ring B.
- Connectivity in Pyridine Rings.

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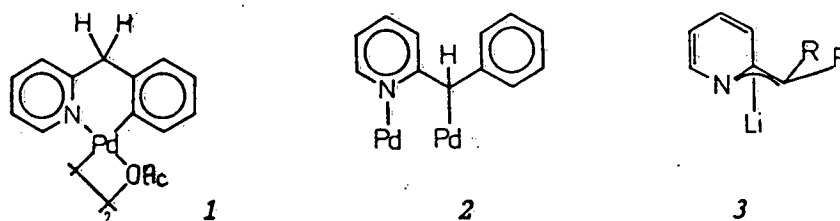
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CHAPTER SIX

PREPARATION OF SOME ORGANOPALLADIUM(II) COMPLEXES.*

6.1 Introduction

The ligand 2-benzylpyridine, pyPhCH_2 , orthometallates on reaction with palladium(II) acetate to give a dinuclear arylpalladium complex containing the ligand as a bidentate chelating anion ($N,C(\text{aryl})$), **1**¹. However, deprotonation of the methylene linkage occurs on reaction with strong bases such as n-butyllithium giving the anion pyPhHC^- , and the subsequent reaction of this anion with palladium(II) substrates leading to formation of dinuclear alkylpalladium complexes bridged by the ligand, ($N,C(\text{alkyl})$), **2**, is described in this chapter.²

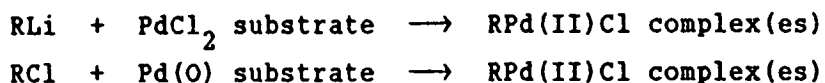


Attempted orthometallation of the related ligands py_2CH_2 and $\text{py}_n\text{Ph}_{3-n}\text{CH}$ ($n = 1-3$, Chapter 3) has only resulted in isolation of an organometallic complex of the ligand pyPh_2CH , of similar structure to **1** (see page 61). Thus, as each of the ligands py_2CH_2 and $\text{py}_n\text{Ph}_{3-n}\text{CH}$ may be deprotonated by n-butyllithium, or halogenated at the bridging carbon atom, attempted formation of other Pd-C(alkyl) complexes similar to **2** is also described. Allylic bonding may also be possible since studies of related ligands containing a deprotonated α -picolyl moiety in the form $\text{py}(\text{Me}_3\text{Si})_n\text{H}_{2-n}\text{C}^-$ ($n = 1,2$) with lithium, copper(I), and silver(I), have shown that in both the solution and solid states bonding modes similar to **2** and **3** may occur.³⁻⁵

Two synthetic routes are described here to give complexes similar to **2** and/or **3** - reaction of deprotonated ligands with

* Some published material concerning this work appears in Publication 2 page 222.

palladium(II) halide substrates, and oxidative addition of ligand halides to palladium(0) substrates.



Whether formation of organopalladium(II) complexes is attempted via organolithium reagents with Pd(II) substrates or via oxidative addition of ligand halides to Pd(0) substrates, the choice of ancillary donor groups associated with palladium is crucial to any further study of complex reactivity. The ancillary ligands generally available to form neutral monomeric palladium(II) halide substrates suitably inert toward lithium reagents generally possess phosphine, nitrogen (aromatic), or sulfur (thioether) donor groups, for example, $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$, $[(\text{py})_2\text{PdCl}_2]$, and $[(\text{Me}_2\text{S})_2\text{PdCl}_2]$, respectively.

To preserve the capacity for donor displacement reactions in products, phosphine ligands as ancillary donors have been avoided in the choice of Pd(0) and Pd(II) substrates. For reasons of expected product instability thioether donors have also been avoided in the choice of Pd(II) substrates. Thus, for reaction of lithio-ligands with palladium(II) halide the substrate *trans*-bis(4-methylpyridine)palladium(II) chloride,⁶ *trans*- $[(\gamma\text{-pic})_2\text{PdCl}_2]$, was chosen*, and for reaction of ligand halides the palladium(0) complex $[(\text{dba})_2\text{Pd}]$ was chosen.

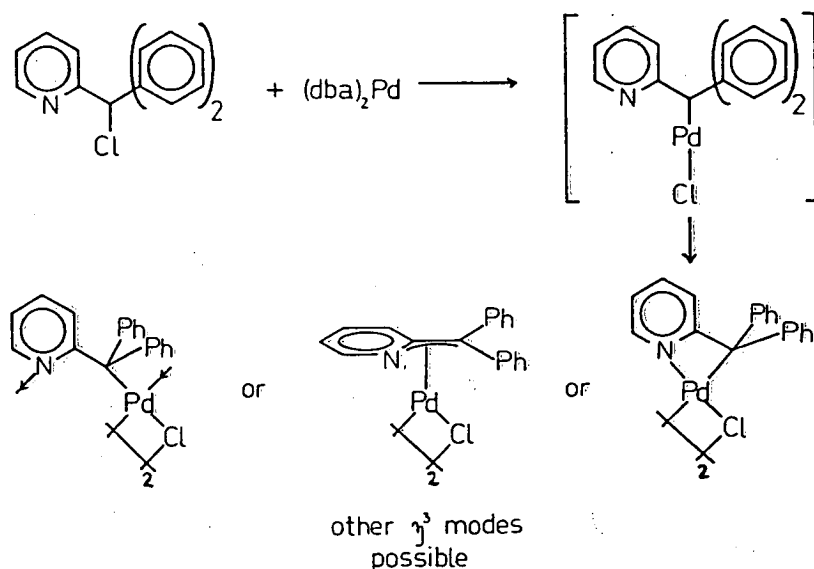
Although all ligands of interest to this study could be obtained as their lithio- derivatives, preliminary reactions between lithio-ligands and *trans*- $[(\gamma\text{-pic})_2\text{PdCl}_2]$ were complicated by the insolubility of the palladium substrate, and substantial reduction of substrate and/or products was observed. Thus, oxidative addition reactions of ligand halides to Pd(0) were attempted where possible.

In the series $\text{py}_n\text{Ph}_{3-n}\text{CCl}$ ($n = 1-3$), only pyPh_2CCl ($n = 1$) and py_3CCl ($n = 3$) have previously been reported (see page 157), and thus py_2PhCCl ($n = 2$) has been prepared for this study (see

* 4-methylpyridine was chosen in preference to pyridine as the methyl substituent is readily discerned by ¹H nmr spectroscopy.

page 208). However, for py_2HCCl very low stability (presumably towards quaternisation) has been reported,⁷ and thus, preparation of the ligands $\text{py}_n\text{Ph}_{2-n}\text{HCCl}$ ($n = 1, 2$) was not attempted.

The reaction between pyPh_2CCl and $[(\text{dba})_2\text{Pd}]$ is donor-deficient*, so that dimerisation or polymerisation may be expected, and other bonding modes, including the formation of an η^3 -allylic bond, are more likely than from $\text{trans}[(\gamma\text{-pic})_2\text{PdCl}_2]$ as a substrate. Examples of some possible bonding modes of pyPh_2C^- are given in Scheme 1.

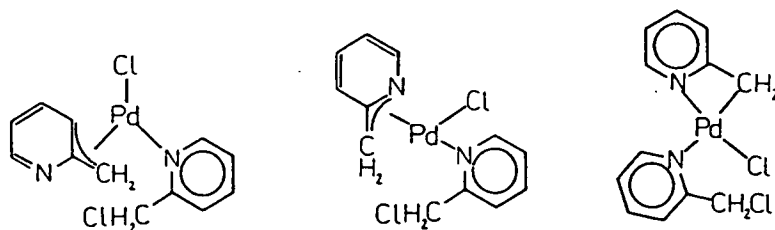


Scheme 1

Hitherto, no precedent for structural units involving $\overline{\text{PdNCC}}$ four-membered rings is available but the reported reaction product of the condensation between 2-chloromethylpyridine with palladium vapours may involve this feature.⁸ The authors⁸ suggest, on the basis of analytical results and I.R. spectra, that three structural possibilities exist and that, "An alternate structure involving a C-Pd σ -bond is also possible, although the

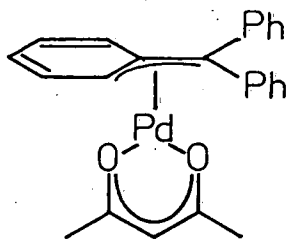
* The term "donor-deficient" will be used to describe a reaction where insufficient σ -donors, (C,N,Cl, etc.), are present to fill all available coordination sites to form a square-planar monomer containing a Pd-C σ -bond.

formation of a four-membered ring would not seem likely."*



In the course of this study a complex containing this structural feature has been isolated and characterised by X-ray crystallography (see page 142).

The allylic structure shown in Scheme 1 bears substantial similarity to the product of the donor-deficient reaction between triphenylmethylchloride (Ph_3CCl) and $[(\text{dba})_2\text{Pd}]$ (or $[(\text{dba})_3(\text{solv.})\text{Pd}_2]$) which yields an unusual allylic complex, presumably a dimer, which has been characterised as its monomeric acetylacetonato- derivative.^{9,10}

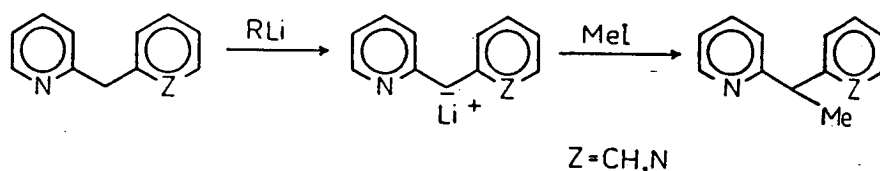


A solid state study of the monomeric complex has been reported¹⁰ and studies in solution have revealed a variety of fluxional processes⁹ (see page 133 for further discussion). Solution studies of related complexes containing a para substituent on one of the phenyl rings have given some insight into the bonding preference with respect to the electron releasing or withdrawing effect of this substituent.⁹ A strong preference for palladium binding to the more electron rich aromatic ring has been established.

* The product was assumed to be monomeric although no molecular weight nor ^1H or ^{13}C nmr information was presented.

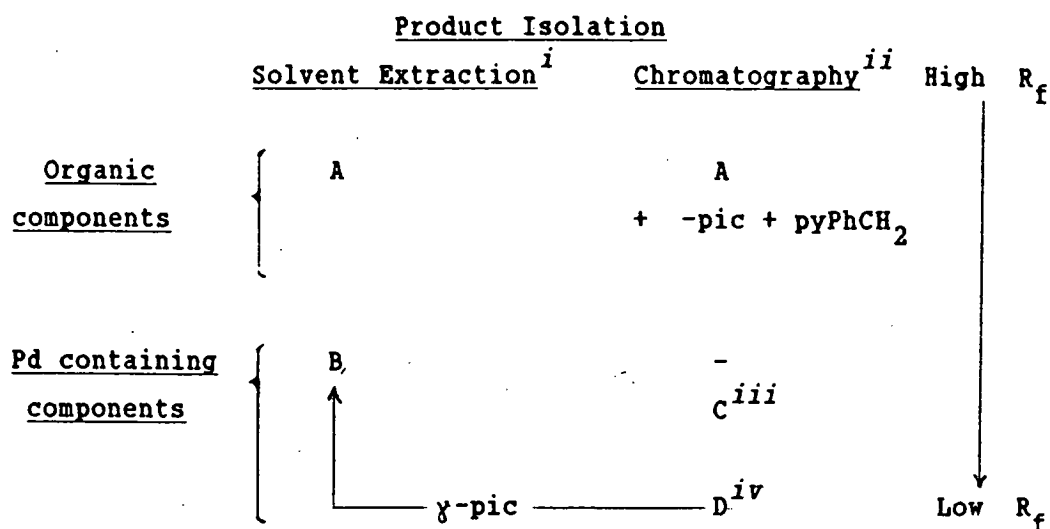
6.2 The Reaction Between Lithiated Ligands and a Palladium(II) Chloride Substrate.

The ligands pyPhCH_2 and py_2CH_2 react with butyllithium to form the strongly coloured red/orange salts $\text{pyPhHC}^-\text{Li}^+$ and $\text{py}_2\text{CH}^-\text{Li}^+$, respectively. At 0°C the lithiation appears to be virtually quantitative as indicated by the yield of methylation products on their reaction with methyl iodide (see Experimental page 209 and 211).



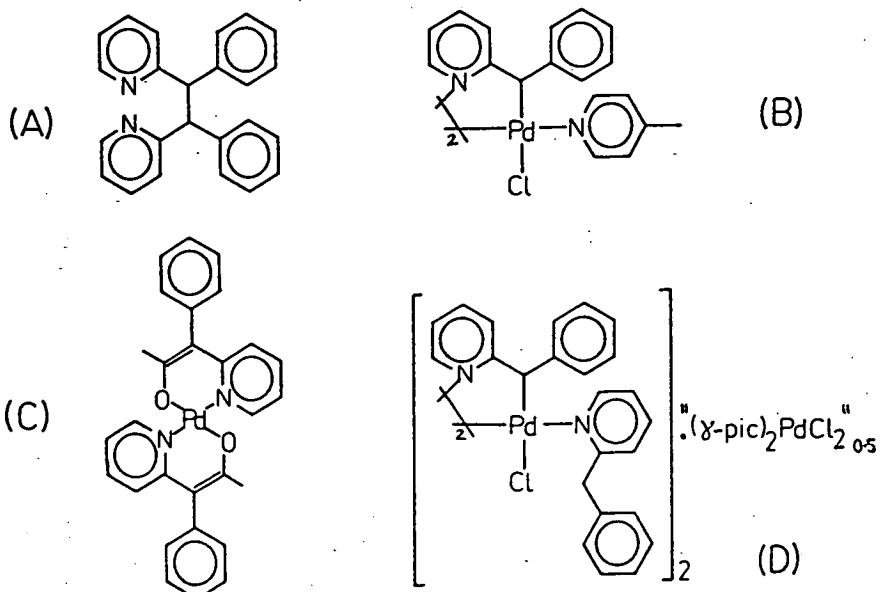
Investigation of reactions of the anions pyPhHC^- and py_2HC^- with *trans*- $[(\gamma\text{-pic})_2\text{PdCl}_2]$ have been attempted by lithiation of the ligands (in Et_2O and THF, respectively) and slow addition of the lithio-ligand to a suspension of *trans*- $[(\gamma\text{-pic})_2\text{PdCl}_2]$ in diethyl ether at low temperature (Experimental page 197). In both instances the reactions produce substantial quantities of reduced palladium, traces of dimerised ligands of the form $(\text{pyPhHC})_2$ and $(\text{py}_2\text{HC})_2$, previously isolated from related reactions with HgI_2 (page 95), starting materials and their decomposition products, as well as isolable organometallic complexes in low and variable yield from the reaction with pyPhHC^- . No organometallic complexes have been obtained from the reaction of py_2HC^- with *trans*- $[(\gamma\text{-pic})_2\text{PdCl}_2]$.

The reaction between $\text{pyPhHC}^-\text{Li}^+$ and *trans*- $[(\gamma\text{-pic})_2\text{PdCl}_2]$, followed by hydrolysis, produces a number of products, and differing products are obtained from solvent extraction methods compared with chromatographic techniques, schematically illustrated below. In each instance the crude product mixture was obtained by isolation of the organic phase and combination of this solution with further chloroform extracts of the hydrolysate. After drying of the organic extracts and removal of solvents a red/orange oily mixture was obtained containing some crystalline solids. The two separation methods were then applied directly to this material.



- i) product (A) crystallises from a hexane extract of the crude reaction product, and product (B) from dichloromethane/acetone.
- ii) Medium pressure, silica gel, CHCl₃/4% - ethylacetate elution.
- iii) from reaction with chromatographic solvent, ethylacetate.
- iv) low R_f material is composed of two or more components.

Product (A) has been identified as the dimeric coupling product (pyPhHC)₂ by comparison (I.R., ¹H nmr) with a pure sample prepared by other means (page 194), and products (B) and (C) have each been the subject of X-ray crystallographic analysis.²⁸

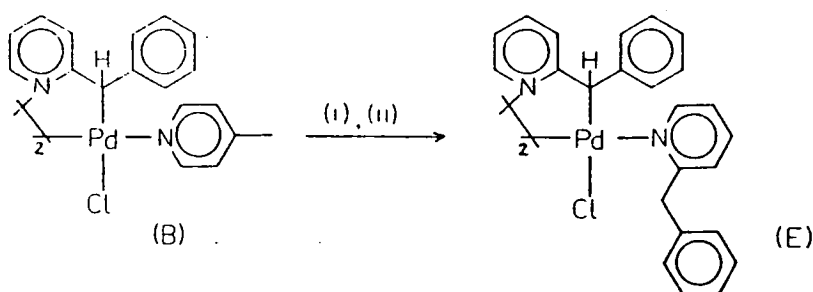


Product (D) has been assigned the empirical formula above where " $(\gamma\text{-pic})_2\text{PdCl}_2$ " has been included to account for microanalytical figures, but is *not* necessarily a molecule of starting material.

Differences in isolation technique account for the differences observed in isolated products. Advantageously, chromatographic separation allows ready isolation of minor components and allows rapid physical separation of purely organic products from inorganic and organometallic products by virtue of large differences in R_f values, although the actual length of time for elution may be long. In contrast, isolation of products using solvent extraction methods is rarely as selective in complete removal of product components, and thus, prolonged contact of species occurs. A disadvantage of the chromatographic technique arises from the necessity to increase solvent polarity, as frequently the palladium containing complexes of interest have low R_f values. Increasing solvent polarity requires the use of polar solvents that may in turn react with compounds of interest.

Low R_f material from the reaction between $\text{pyPhHC}^-\text{Li}^+$ and $\text{trans}-[(\gamma\text{-pic})_2\text{PdCl}_2]$, designated *fraction (D)*, gave small quantities of red/orange crystals from acetone, designated *product or complex (D)*, although the bulk of the material could not be induced to crystallise by this means. Treatment of the whole crude fraction with an excess of $\gamma\text{-pic}$ yielded complex (B) in a similar yield to that obtained via solvent extraction, 32% and 28%, respectively. Thus, some components, other than (B), that comprise the fraction may also share the bridging deprotonated 2-benzylpyridine group as a common structural unit.

Under appropriate conditions this type of exchange process may be reversed, and, for example, complex (B) has been used to generate the dimer (E), below. This dimer represents the dimeric organometallic component contained within *complex (D)* which could not be liberated from associated inorganic material by either chromatography or repeated recrystallisation (see page 123 for further comment).



(i) excess 2-benzylpyridine, (ii) slow distillation of volatile products.

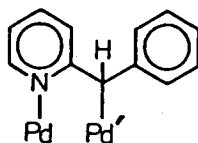
The very minor component (C) represents a reaction product between an unidentified palladium species with ethylacetate (elution solvent).

The coupling product (A) may arise from reduction of a number of species, but presumably where 2-benzylpyridine is bound to palladium via a σ - or π -allylic bond.

6.2(i) The Solid State Structure of $[(\mu\text{-py-}M)(\text{PhHC-C})](\gamma\text{-pic-}M)\text{PdCl}]_2 \cdot \text{CH}_2\text{Cl}_2$, Complex (B).²⁸

Crystals of the title complex suitable for X-ray crystallographic study were obtained by recrystallisation from dichloromethane/acetone.

Two deprotonated 2-benzylpyridine ligands link the palladium atoms as shown schematically below. The dimeric complex has minor differences in coordination geometry for the two palladium atoms, Pd and Pd'.



Square-planar coordination about palladium is based on a *trans* arrangement of nitrogen donors. Bond angles about the palladium atoms range from $87.7(1) - 94.0(2)^\circ$ with maximum deviation from the mean planes 'PdN₂CCl' observed for the γ -pic nitrogen atom bound to Pd' (0.14\AA). The palladium atoms are $3.062(7)\text{\AA}$ apart and details of the local environments about Pd and Pd' are given in Table 6.1.

The structure of the complex involves similar structural features to those reported for the oxidative addition product formed on reaction between pyCH_2Cl and $[(\text{Ph}_3\text{P})_4\text{Pd}]^{11}$ (overleaf).

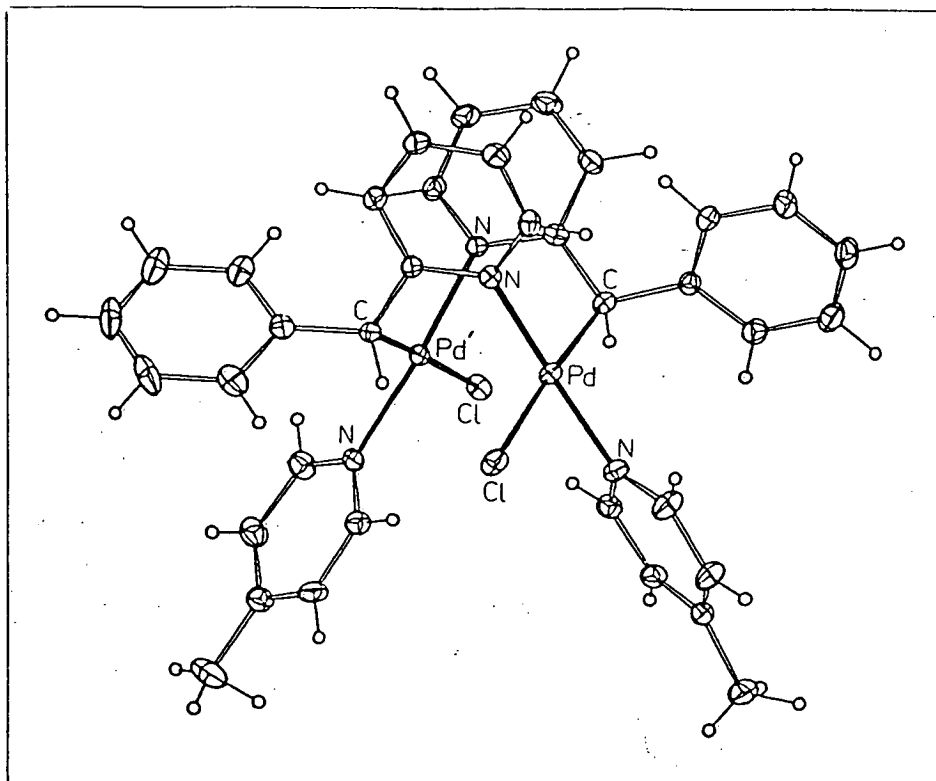
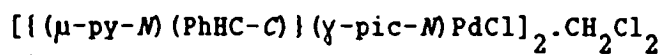
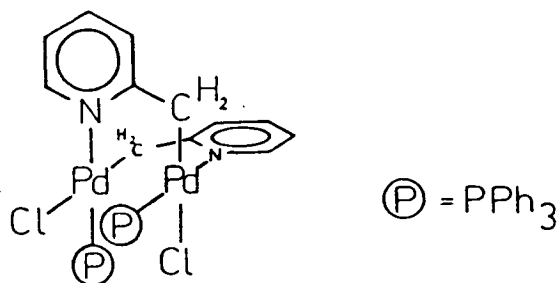


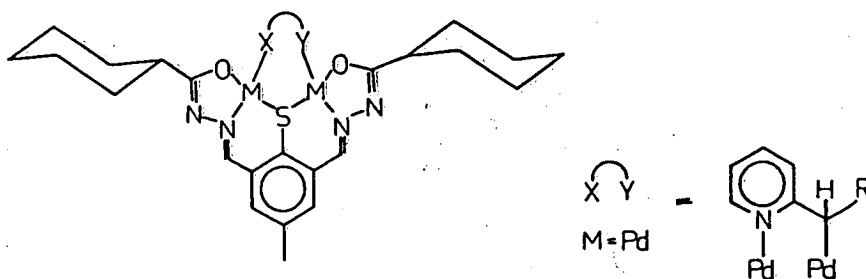
Table 6.1 Palladium Environments

Atoms	Pd	Pd'
Distances (Å)		
Pd-Cl	2.430(2)	2.446(2)
Pd-C	2.070(6)	2.079(5)
Pd-N _*	2.046(4)	2.029(5)
Pd-N	2.049(4)	2.041(5)
Pd-Pd'	3.062(7)	
Angles (degrees)		
Cl-Pd-C	177.0(2)	178.1(2)
Cl-Pd-N _*	91.1(1)	87.7(1)
Cl-Pd-N	87.6(1)	89.9(1)
C-Pd-N _*	91.7(2)	94.0(2)
C-Pd-N _*	89.5(2)	88.6(2)
N-Pd-N	176.7(2)	172.1(2)

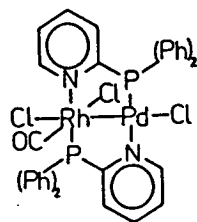
* nitrogen atom in 4-methylpyridine (γ -pic.)



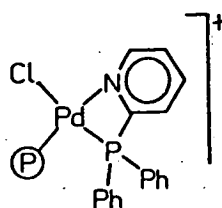
The bridging mode of the α -picolyl moiety has also been investigated in conjunction with the use of large binucleating ligands,² and a similar bridging mode is observed for inorganic complexes of (pyridin-2-yl)phosphines, in particular, pyPh_2P .¹²⁻¹⁵ This phosphine ligand also has the capacity to act as a bidentate chelate forming four-membered rings.^{14,16}



(Ref. 2)



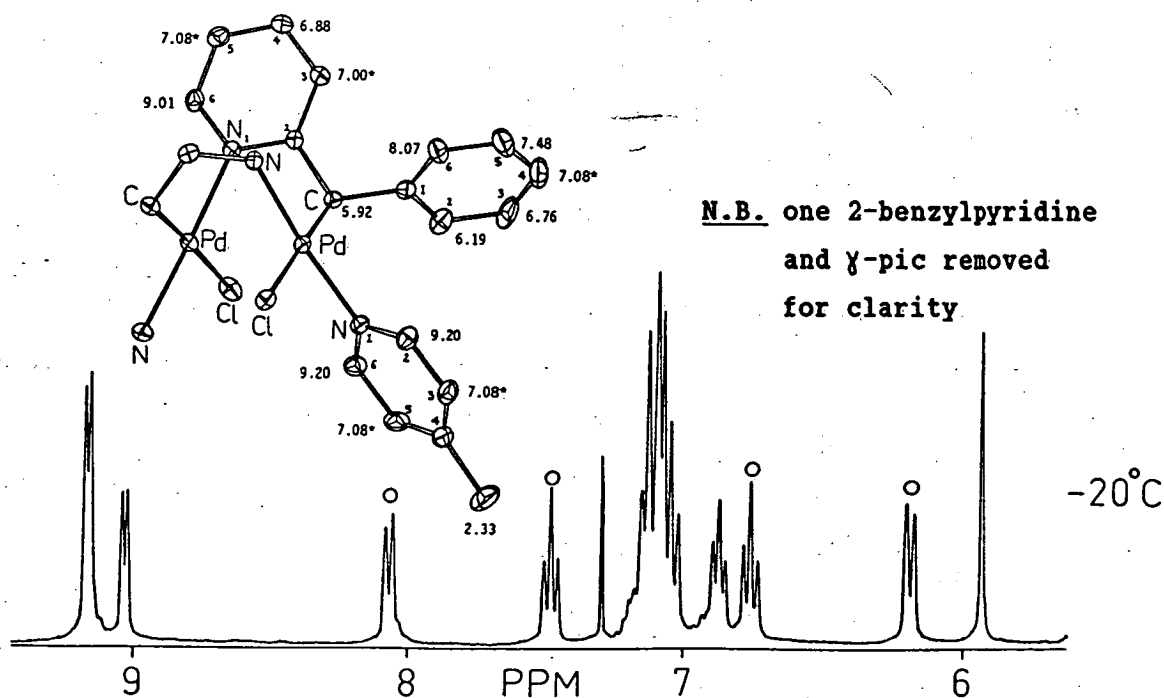
(Ref. 12)



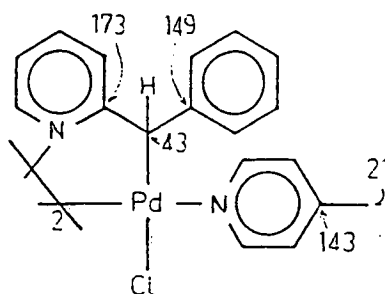
(Ref. 16)

6.2(ii) Nmr Characterisation of Complex (B)

The standard ^1H nmr spectrum of $[(\mu\text{-py-}M)(\text{PhHC-C})(\gamma\text{-pic-}M)\text{PdCl}]_2 \cdot \text{CH}_2\text{Cl}_2$ at ambient temperature consists of both sharp and broadened resonances. Pyridine H(6) and methyl resonances associated with $\gamma\text{-pic}$, and pyridine H(6) and methine CH resonances associated with 2-benzylpyridine, are sharp. Thus, broadened resonances in the aromatic region are directly attributable to the phenyl group of 2-benzylpyridine. The possibility of monomer/dimer equilibria may be excluded as molecular weight determination on complete removal of dichloromethane (0.1 mm, 70°C , 30h, ^1H nmr detection) indicates a dimeric formulation (found 792, calc. 806). The COSY spectrum of the complex obtained at -20°C has allowed full proton assignment of the standard spectrum below (aromatic region). At -20°C the five phenyl ring proton environments are all clearly separated, indicative of frozen rotation on the nmr time scale. The furthest upfield phenyl proton resonance (6.19 ppm) has been attributed to the 2-benzylpyridine pyridine H(2) atom, in close proximity to $\gamma\text{-pic}$. In contrast, the hydrogen atom H(6) on the phenyl ring appears as the furthest downfield phenyl resonance (8.07 ppm) from COSY spectroscopy.¹⁷



The ^{13}C nmr spectrum (^1H decoupled at -20°C) shows the expected sixteen lines including three quaternary carbon atoms, one methine, and one methyl carbon (using DEPT sequences¹⁷). The quaternary, methine and methyl carbon resonance assignments are shown below. Full carbon assignment using $^{13}\text{C} - ^1\text{H}$ correlation spectroscopy was not possible for this complex as temperature stability for the acquisition time (ca. 20h) could not be maintained.



6.2(iii) Solid State²⁸ and Solution Structure of $[\{\text{pyPhC:C(Me)O-N,O}\}_2\text{Pd}]$, Complex (C).

On isolation of fraction C from the hydrolysate described on page 112 and crystallisation from acetone/dichloromethane complex (C) was obtained as a highly crystalline orange solid. The standard ^1H nmr spectrum exhibited resonances typical of 2-benzypyridine in the aromatic region as well as a signal at 1.85 ppm, initially assumed to be traces of absorbed water. After collection and combination of this minor fraction, crystallised in the same manner from a number of preparations, efforts to remove the "water" failed. Infrared spectra obtained for a number of samples demonstrated the absence of water of hydration. Surprisingly, no methine resonances associated with the ligand could be detected in the ^1H nmr spectrum, and the absence of γ -pic was conclusively demonstrated. The absence of halogen was confirmed by X-ray microprobe analysis.

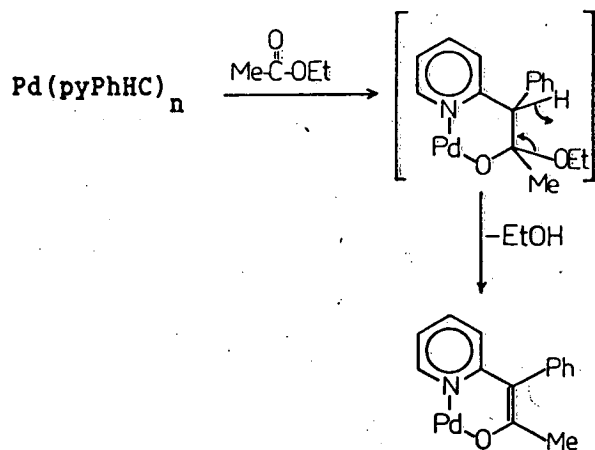
Mass spectroscopic molecular weight determination suggested a molecular mass of ca. 527* (an isotopic cluster of seven

* No solvent molecules, e.g., acetone or dichloromethane, were evident.

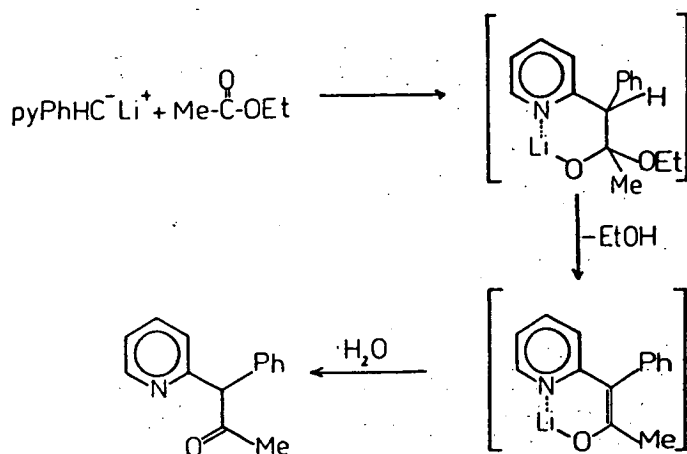
lines), and this was in agreement with the osmometric molecular weight determination which gave a molecular mass of 530 (ca. $3 \times 10^{-2} M$ in CHCl_3).

A ^{13}C nmr spectrum was obtained showing twelve chemically distinct carbon atom environments including four quaternary carbons as well as a methyl carbon atom.

Since no formulation could be proposed that would adequately account for the information obtained, a crystal structure determination was performed on the product. The structure (page 122) clearly indicates that a reaction has occurred between a palladium complex and ethylacetate, used to increase solvent polarity in chromatographic separation.



The species isolated suggests that a small component of the reaction mixture undergoes a reaction similar to that reported between $\text{pyPhHC}^-\text{Li}^+$ and a range of esters including ethylacetate.¹⁸



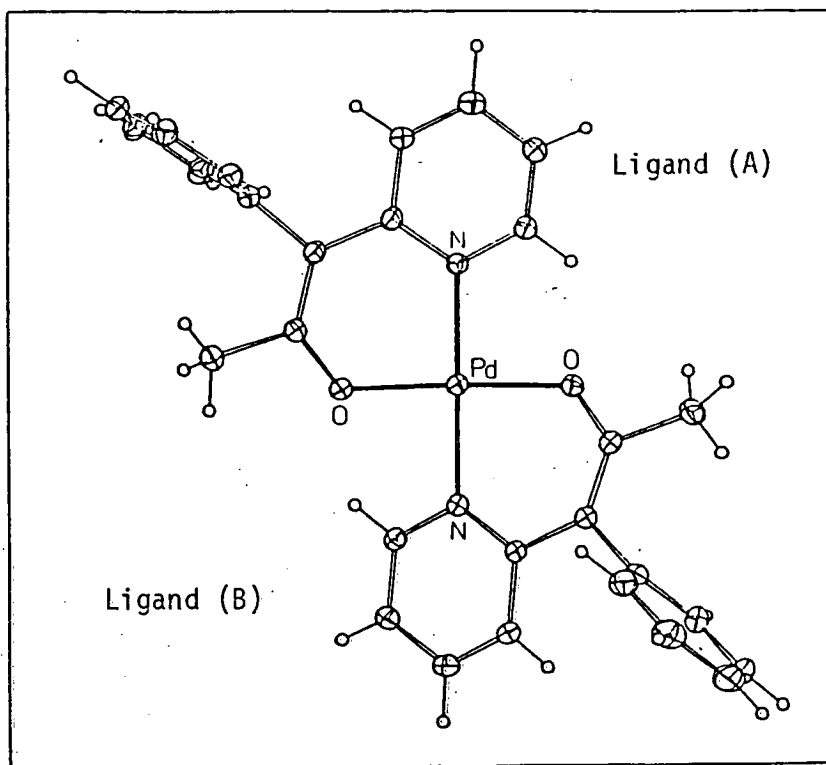
The palladium(II) complex closely resembles the second intermediate structure proposed in the acylation process above.

Full assignment of all proton resonances for the complex has been enabled by COSY spectroscopy, and in turn full carbon resonance assignment has been possible using standard ^{13}C and $^{13}\text{C} - ^1\text{H}$ correlation spectroscopy.¹⁷

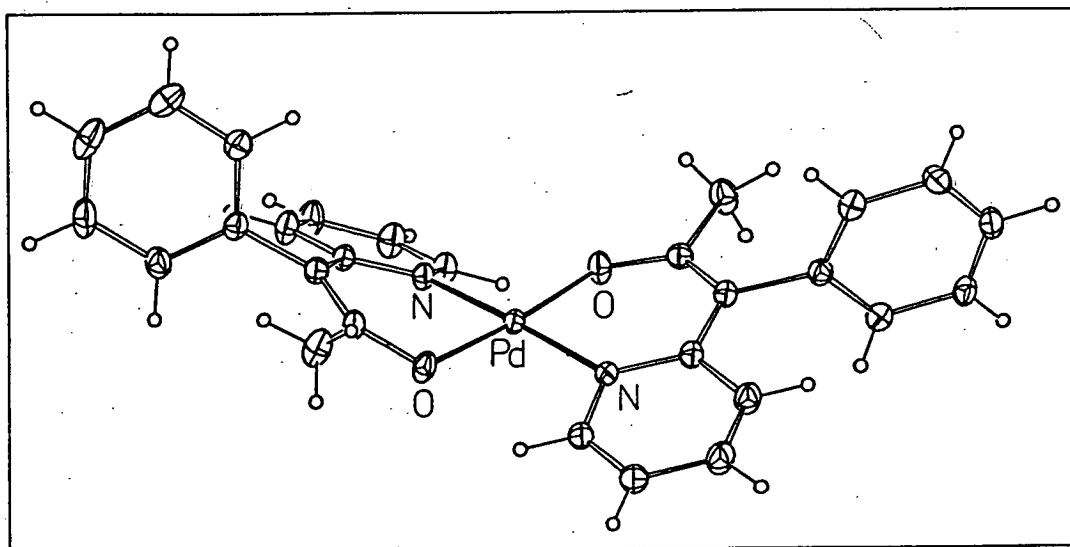
The solid state structure of complex (C) overleaf shows that square-planar geometry about palladium is attained via a *trans* arrangement of oxygen and nitrogen donor atoms where the angles $\text{N(A)}-\text{Pd}-\text{N(B)}$ and $\text{O(A)}-\text{Pd}-\text{O(B)}$ are $176.1(2)^\circ$ and $175.8(1)^\circ$, respectively. The six membered (O,N) chelate rings subtend O-Pd-N angles of $91.7(1)^\circ$ (A) and $89.2(1)^\circ$ (B) with average Pd-O and Pd-N bond lengths of $1.967(3)$ and $2.036(4)\text{\AA}$, respectively. Puckering of the chelate rings results in the pyridine rings subtending dihedral angles of 13.8° (A) and 27.9° (B) to the plane defined by ' N_2O_2 ' (Pd deviation 0.004\AA). The phenyl substituents subtend dihedral angles of 82.5° (A) and 82.0° (B) to ' N_2O_2 ' which is also apparently that orientation present in the solution structure since the pyridine H(3) proton is substantially shielded by this substituent and resonates at 6.41 ppm.

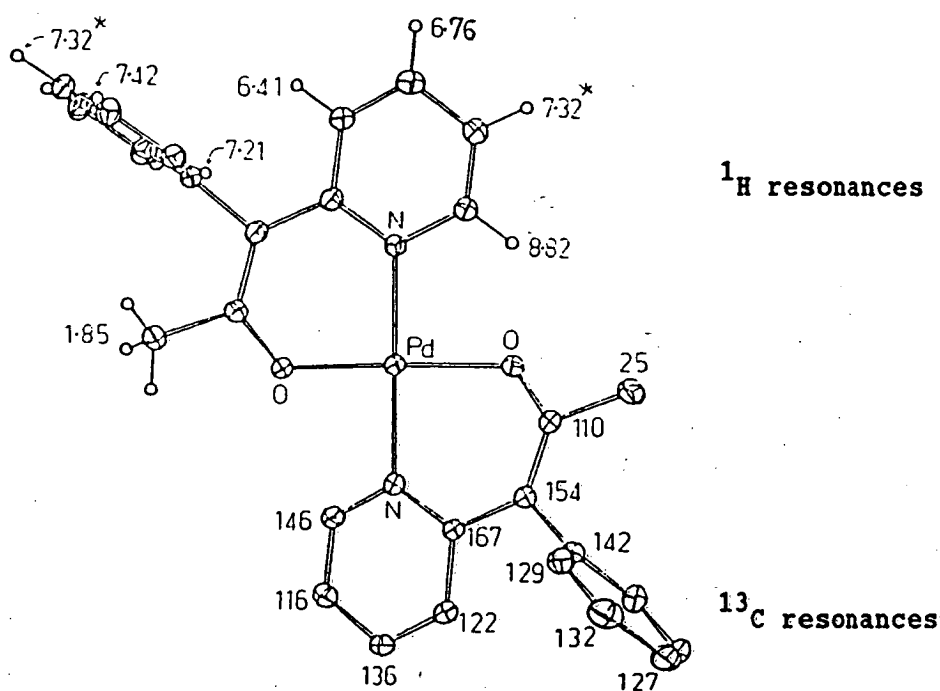
Bond lengths within the six-membered chelate ring are consistent with delocalisation. For example, the pyridine C(2)-C(α) (average) bond length of ca. 1.45\AA is shorter than the phenyl C(1) - C(α) bond, 1.51\AA , where C-C single and double bonds are usually ca. 1.53 and 1.34\AA , respectively.²³ Similarly, the observed C-O bond length of ca. 1.31\AA is comparable to that expected for a double bond, 1.29\AA .²³

$[\{\text{pyPhC}:\text{C}(\text{Me})\text{O}-\text{N},\text{O}\}_2\text{Pd}]$ Viewed Normal to the Square Plane



$[\{\text{pyPhC}:\text{C}(\text{Me})\text{O}-\text{N},\text{O}\}_2\text{Pd}]$ Viewed Normal to the Phenyl Ring of
Ligand B.



Nmr Chemical Shifts

* estimated positions in a multiplet

6.2(iv) The Structures of Complex (D) and

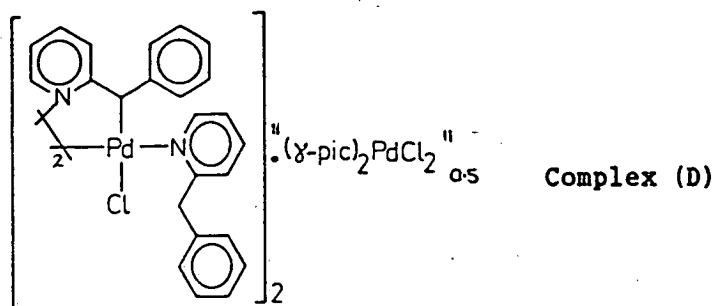
$[(\mu\text{-py-M})(\text{PhHC-C})](\text{pyPhCH}_2\text{-M})\text{PdCl}]_2$, Complex (E).²⁸

The ¹H nmr spectra of complexes (B) and (D) and (E), (page 118 and 125, respectively) share the common feature of a singlet methine resonance at ca. 6.1 ppm indicative of 2-benzylpyridine σ-bound to palladium through C(α). The solid state structures of (E) (page 129) and (B) (page 116) both exhibit pyPhHC⁻ units linking two palladium atoms, and thus, this structural feature is also presumed to be present in complex (D).

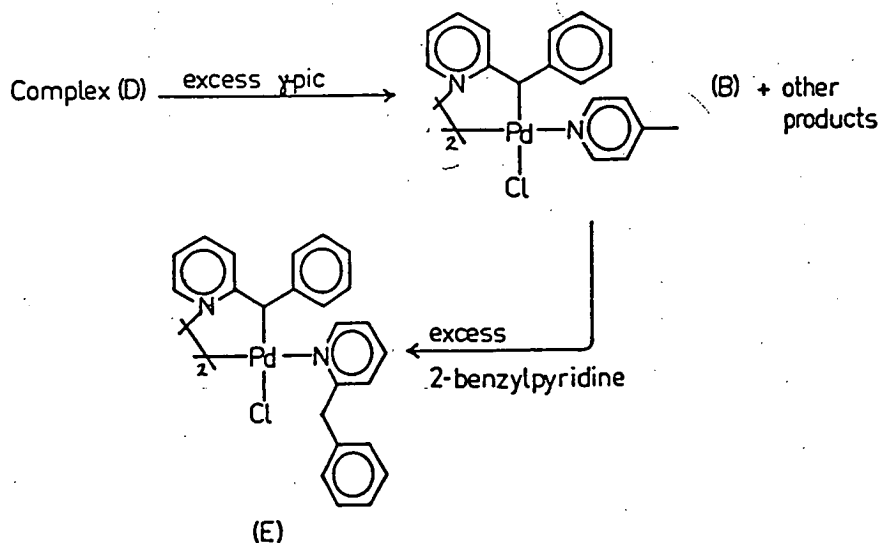
The ¹H nmr spectrum of (D) is more complex than that of (E) where added signals arise from two γ-pic groups in different environments. Both microanalytical results and integration values suggest that complex (D) is composed, in 2:1 ratio, of an organometallic component similar to (E) in association with an

inorganic component of *stoichiometry* $(\gamma\text{-pic})_2\text{PdCl}_2$. However, the inorganic component is *not* assumed to be a molecule of the starting material $\text{trans}[(\gamma\text{-pic})_2\text{PdCl}_2]$ since only one $\gamma\text{-pic}$ environment would be expected for this molecule.

The organometallic component within (D) could not be successfully separated from the inorganic component by either repeated recrystallisation or by chromatographic means.

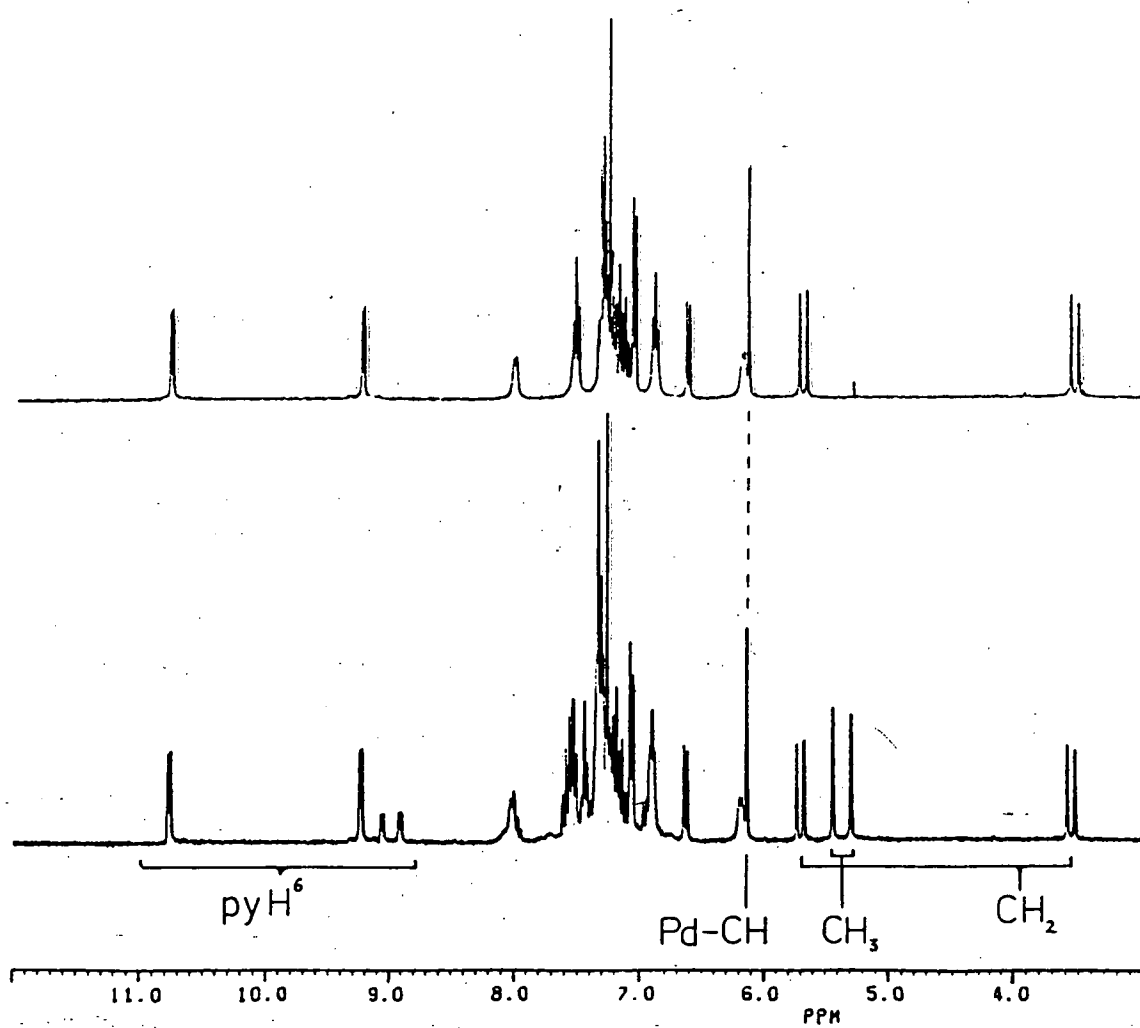


However, complex or fraction (D) (see page 114) may be used to generate complex (B) via donor displacement thus removing inorganic materials. In turn, the thermally robust complex (B) may be used to synthesise complex (E).



The spectrum of complex (E), overleaf, shows two distinct pyridine H(6) environments originating from 2-benzylpyridine and deprotonated 2-benzylpyridine, a sharp methine proton resonance

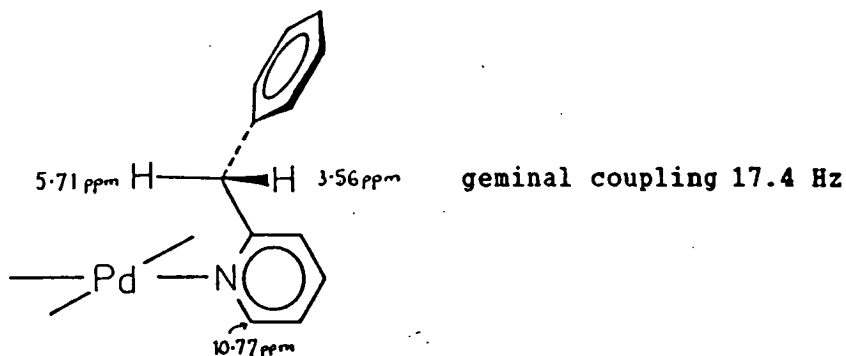
^1H nmr Spectra of Complexes (D) (lower) and (E) (upper).



at 6.14 ppm, and two substantially separated geminal (coupled) methylene proton environments. COSY spectroscopy, and comparison with complex (B), has allowed assignment of chemical shift values of the majority of proton signals.

Complex (E) exhibits some broadened aromatic resonances at room temperature that sharpen at -20°C . These resonances have been assigned to the phenyl substituent of the bridging deprotonated 2-benzylpyridine group by their expected similarity to related resonances in complex (B). The separation of the five phenyl group resonances in (E) has also been attributed to hindered rotation of this substituent.

In contrast to complex (B) containing a γ -pic N-donor, the 2-benzylpyridine N-donor in (E) has restricted motion due to the bulky benzylic substituent at the 2-position of the pyridine ring. As a result of this hindered motion, the two methylene protons on the bridging carbon group experience markedly different fields. Contributions to the large chemical shift difference (2.15 ppm) presumably arise from both an intrinsic difference in proton environments due to the asymmetric substitution in the square plane about palladium, as well as Pd...H interaction. That proton furthest downfield (5.71 ppm) presumably resides close to the axial position of a palladium atom, while the second, remote from the metal, resonates at 3.56 ppm similar to that found for the free ligand (4.12 ppm). The downfield shift observed for the related pyridine H(6) proton (resonating at 10.77 ppm) is also a result of proton axial proximity to the metal center. It has been noted that, "The downfield shifts for nuclei in the regions close to the vacant fifth and sixth coordination sites of square-planar d^8 complexes are due to paramagnetic anisotropy^{20,21} of the metal atom and increase with decreasing Pd-H distance, reaching a maximum when the Pd-H vector is perpendicular to the coordination plane".¹⁹ In complex (E) a conformation in solution similar to that below is suggested, where the pyridine ring is approximately normal to the mean square plane about palladium.



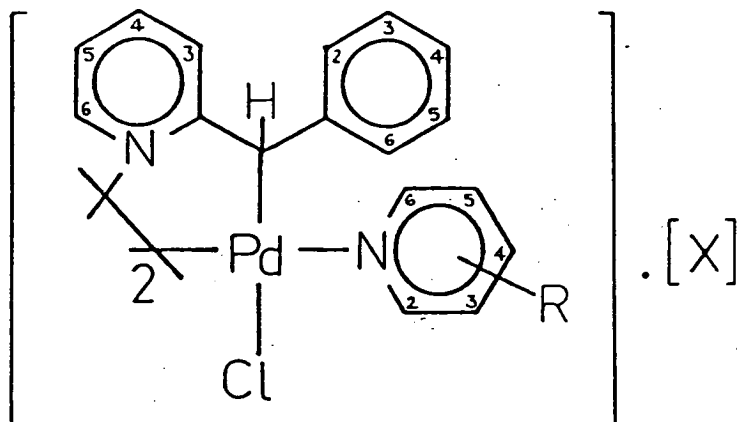
The phenyl group resonances of N-coordinated 2-benzylpyridine occur in the range 7.4 - 7.1 ppm, but cannot be readily assigned due to extensive overlap of resonances in the region.

Compiled proton shift values for complexes (D) and (E) are shown overleaf, where values for complex (B) are included for comparison.

The ^1H nmr resonance signals of complex (D) associated with deprotonated 2-benzylpyridine and N-bound 2-benzylpyridine are directly comparable to those of complex (E) and have been assigned in an analogous manner. Additional signals arising from occluded inorganic material display two H(6,2) resonances for γ -picoline donors at 9.06 ppm and 8.91 ppm, coincident H(5,3) resonances estimated to occur at ca. 7.25 ppm from the COSY spectrum, and two methyl signals at 5.44 and 5.30 ppm. A pure sample of the starting material $\text{trans}-[(\gamma\text{-pic})_2\text{PdCl}_2]$ exhibits H(6,2), H(5,3), and methyl resonances at 8.62, 7.12, and 2.39 ppm, respectively.

The solid state structure of (E) is shown overleaf along with details of the palladium environments given in Table 6.2. Two deprotonated 2-benzylpyridine ligands link the palladium atoms Pd and Pd'. The dimeric complex has minor differences in coordination geometries for the two metal atoms. Bond angles within the square planes defined by 'PdN₂CCl' and 'Pd'N₂CCl' range from 87.3(9) - 91.9(6) $^\circ$ with the palladium atoms 3.184(3) \AA apart compared with 3.062(7) \AA for (B), and 2.855(2) \AA for [(p-py-

Proton Chemical Shift Values for Complexes (B), (D) and (E).



		Complex		
		(B)	(D)	(E)
Substituent(R):		4-Me	2-benzyl*	2-benzyl*
μ -pyPhHC:	pyH(6)	9.01	9.24	9.24
	H(5)	7.08	6.93	6.94
	H(4)	6.88	7.16	7.16
	H(3)	7.00	*	*
	: PhH(6)	8.07	8.00	8.02
	H(5)	7.48	7.56	7.55
	H(4)	7.08	7.34	7.34
	H(3)	6.67	6.90	6.93
	H(2)	6.19	6.12	6.18
	CH	5.92	6.04	6.14
py(R):	pyH(6)	8.07	10.76	10.77
	H(5)	7.08	7.25	6.94
	H(4)	-	7.57	7.16
	H(3)	7.08	6.63	6.63
	H(2)	8.07	-	-
(R):	2.23	methylene	methylene	
		5.63	5.71	
		3.43	3.56	
(X):	CH ₂ Cl ₂	$\frac{1}{2}(\gamma\text{-pic})_2\text{PdCl}_2$	-	
	5.16	H(6,2) 9.04, 8.91		
		H(5,3) 7.25		
		4-Me 5.43, 5.30		

* Individual phenyl resonances are overlapping and these obscure some pyridine signals.

N.B. The shift values given have been read directly from COSY spectra, those values not shown could not be deduced with certainty from these spectra.

$M(\text{py}-M(\text{PhC}-\text{C}))\text{PdCl}_2 \cdot [(\text{CH}_3)\text{CO} \cdot \text{CH}_2\text{Cl}_2]_{0.5}$ on page 142. The dihedral angle subtended by the pyridine rings of the deprotonated 2-benzylpyridine groups to ' PdN_2CCl ' is ca. 61° , while pyridine in the N-bound 2-benzylpyridine groups subtends an angle of ca. 75° .

$[(\text{u-py}-M(\text{PhHC}-\text{C}))(\text{pyPhCH}_2-M)\text{PdCl}]_2$, Complex E.

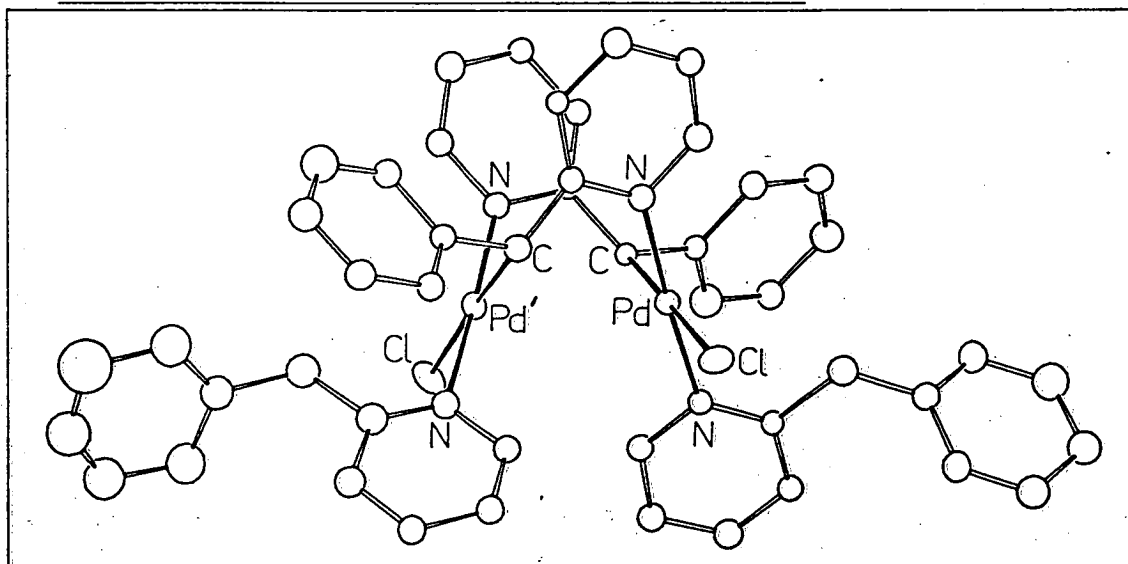


Table 6.2

Palladium Environments

Atoms	Pd	Pd'
Distances (Å)		
Pd-Cl	2.431(8)	2.418(8)
Pd-C	2.13(3)	2.07(2)
Pd-N*	2.04(2)	2.01(2)
Pd-N	1.97(2)	1.99(2)
Pd-Pd'	3.184(3)	
Angles (degrees)		
Cl-Pd-C	177.1(9)	179.0(8)
Cl-Pd-N*	90.2(7)	91.7(6)
Cl-Pd-N	91.9(6)	90.5(6)
C-Pd-N*	87.6(10)	87.3(9)
C-Pd-N	90.4(10)	90.5(10)
N-Pd-N	175.5(9)	175.1(7)

* Nitrogen atom of N-bound 2-benzylpyridine.

Dihedral Angles ($^\circ$) between N-donor aromatic rings and the mean planes defined by ' PdN_2CCl '.

2-benzylpyridine deprotonated	76.6	73.9
2-benzylpyridine	61.8	59.8

6.3 The Oxidative Addition of pyPh_2CCl to Palladium(0).

Oxidative addition of pyPh_2CCl to $[(\text{dba})_2\text{Pd}]$ was performed under anaerobic dry conditions by mixing the ligand and $\text{Pd}(0)$ substrate in benzene and stirring for 20h under a static nitrogen atmosphere at ambient temperature. The resulting deep red solution containing some dark suspended solids was filtered under atmospheric conditions and the filtrate was reduced to dryness under vacuum giving a red/brown residue that crystallised rapidly on standing. The crude product was passed through a medium-pressure silica gel chromatographic column with chloroform elution, and after elution of a yellow band containing free dba (R_f 0.62), an orange band was isolated (R_f 0.14), with a quantity of dark low R_f material remaining. The orange eluent was reduced to dryness giving an orange gum and on addition of a small quantity of acetone the gum rapidly crystallised as a bright orange solid (22%).

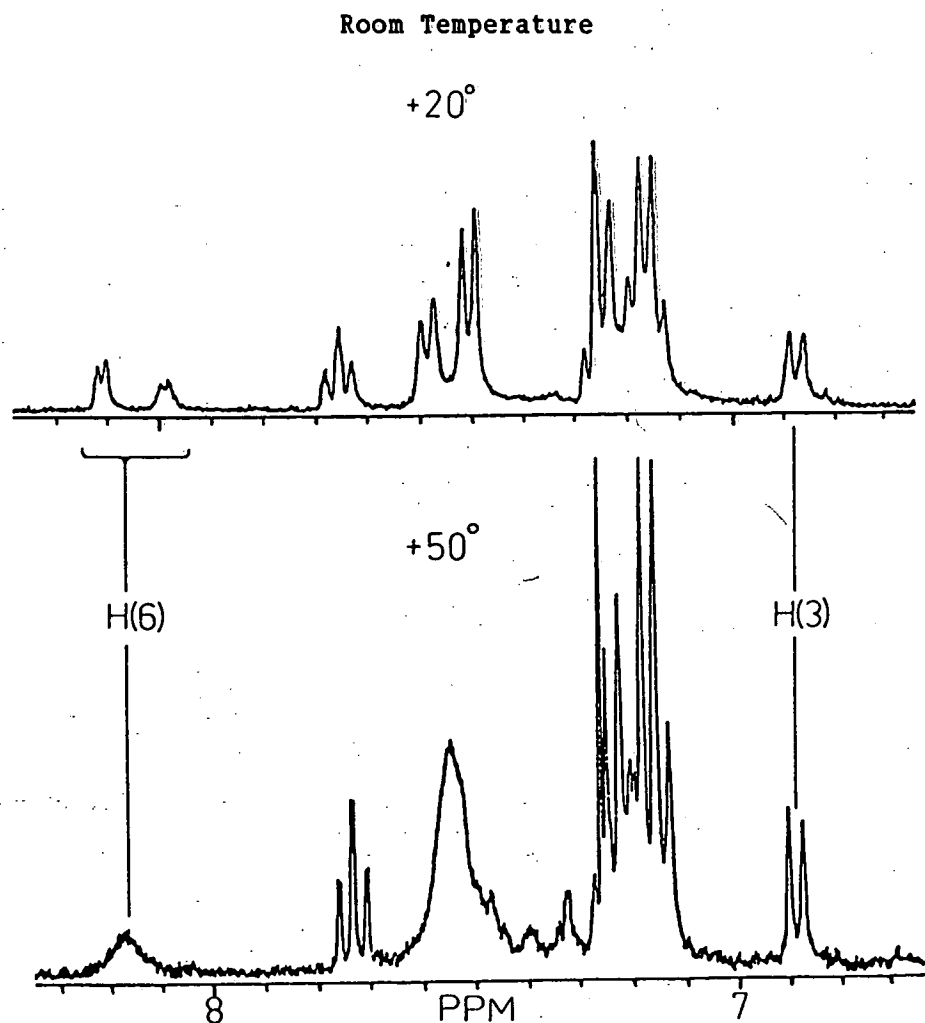
The product is indefinitely stable in the solid state and is moderately soluble in common organic solvents. However, on prolonged standing in chloroform a sparingly soluble yellow precipitate forms and the supernatant solution changes from orange to red. No precipitation of palladium metal occurs during decomposition. The orange solid analysed for $[(\text{pyPh}_2\text{C})\text{PdCl}]_n$ (C,H,N,Cl) and osmometric determination of molecular mass in chloroform indicated a dimeric formulation (found 785, calc. 772). Due to the rapid decomposition of the complex in solution all manipulations and spectral accumulations were carried out as rapidly as possible.

6.3(i) Nmr Characterisation of $[(\text{pyPh}_2\text{C})\text{PdCl}]_2$.

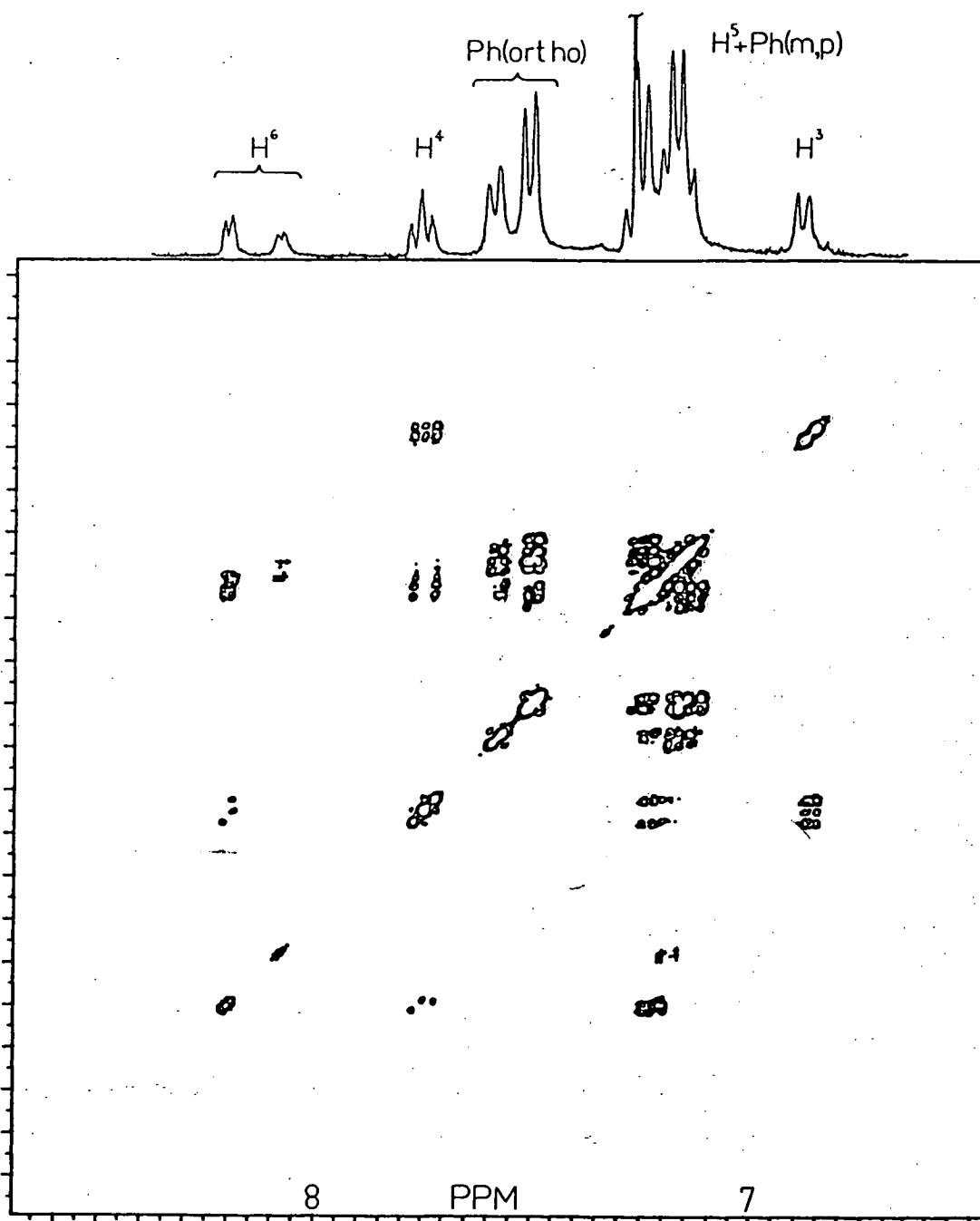
The standard high resolution ^1H nmr spectrum of the complex at 20°C in chloroform consists of slightly broadened aromatic resonances with pyridine H(6) and H(3) environments readily identified as the furthest downfield and upfield resonances, respectively. All other pyridine proton environments have been assigned from the COSY spectrum (page 132). Phenyl proton environments have been deduced from the COSY spectrum, in

conjunction with integration values and expected splitting patterns in the standard spectrum. Thus, the complex exhibits two pyridine H(6) and ortho-phenyl environments, both in 3:2 ratio.

At low temperature (-50°C) the ^1H nmr spectrum remains similar to that obtained at 20°C , but at elevated temperature (50°C) coalescence of divided resonances occurs and remaining resonances sharpen. Prolonged heating of the sample (>15 min) was observed to hasten decomposition but when temperature variation was carried out quickly signal coalescence on heating and redivision on cooling was observed without significant decomposition occurring.

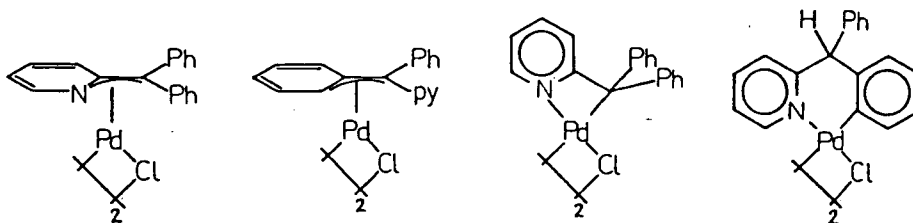


The COSY Spectrum of $[(\text{pyPh}_2\text{C})\text{PdCl}]_2$



Some possible dimeric formulations for the complex involve either a π -allylic (A,B) or σ -bonding mode (C), both empirically similar to a σ -aryl complex (D) previously discussed (page 61).

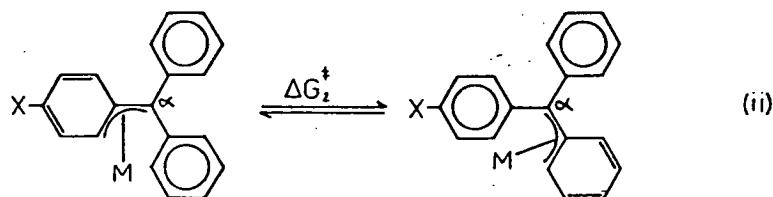
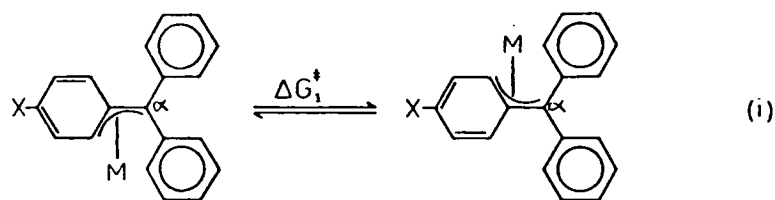
However, as no resonances are observed below 122 ppm in the ^{13}C nmr spectrum (page 139) bonding modes involving C(α) as an sp^3 hybrid (C,D) may be discounted*. Thus, the ligand is allylically bound to palladium (A and/or B).

(A) π -azaallyl(B) π -benzylallyl(C) σ -bonding(D) σ -aryl

The temperature dependent ^1H nmr effects also suggest dynamic behaviour in an allylic dimer, and at least two general interpretations may be used to explain the observed effects. These interpretations are analogous, in part, to fluxional processes established for closely related η^3 -benzylic systems containing Ph_3C^- and some para-substituted derivatives⁹, and thus, a summary of these findings will be presented first.

In the complex $[(\text{Ph}_3\text{C})\text{Pd}(\text{acac})]$ three types of fluxional motion have been observed or inferred, two involving Ph_3C^- , and one involving the ancillary ligand acac^- . Processes involving the aromatic ligand (below) include movement by the metal between two η^3 -positions on a single phenyl ring via suprafacial [1,5]-sigmatropic shifts, (i), and movement by the metal between one aromatic ring and another, (ii).

* sp^3 hybridised carbon atoms in organic molecules commonly resonate in the region 30-20 ppm,²² and C(α) atoms σ -bound to palladium have been found to resonate at 46 and 26 ppm in this study (pages 119 and 145, respectively).



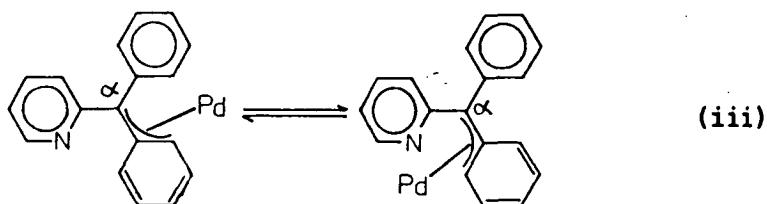
Both processes are manifest in ^{13}C nmr spectra. At -30°C or below process (ii) is slow on the nmr time scale and is not observed. However, process (i) remains sufficiently rapid so that instead of observing fifteen signals in the ^1H decoupled ^{13}C nmr spectrum only eight could be observed (where signal degeneracy occurs in one instance). The averaging effect of process (i) renders C(2) and C(6) of the allylically bound ring equivalent, and the rapid metal shift averages free phenyl ring environments such that the molecule appears to have a plane of symmetry through X (=H) and C(α).

Above -30°C process (ii) becomes rapid on the nmr time scale and produces the net result of averaging C(2) and C(6) resonances of all rings, with C(α) being the only carbon resonance unaffected by the process.

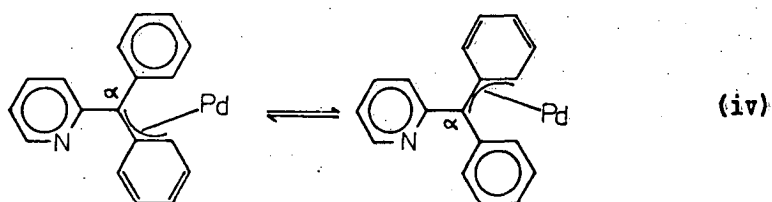
When substituent X is F, Me, or OMe, spectra of greater complexity were obtained although all were adequately described by similar fluxional behaviour. The electron releasing substituents (Me, OMe) were found to favour the binding of the metal to the aromatic ring on which they were situated.

In all instances the number of resonance signals in the ^{13}C nmr spectra indicated that those aromatic groups not involved in allylic bonding were freely rotating about C(1) - C(α). Also, due to extensive accidental degeneracy and averaging effects, observation of fewer signals than expected was frequently noted.

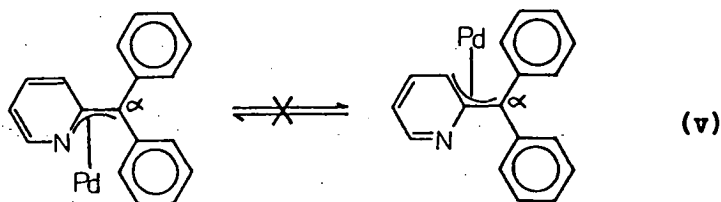
In the complex $[(\text{pyPh}_2\text{C})\text{PdCl}]_2$ η^3 -allylic bonding may involve the pyridin-2-yl and/or the phenyl substituents. If η^3 -benzylallylic bonding occurs then a fluxional process identical to (i) may result in the averaging of C(2) and C(6), and thus H(2) and H(6) environments, (iii).



Similarly, a process identical to (ii) may occur resulting in the equilibration of both phenyl rings, (iv).

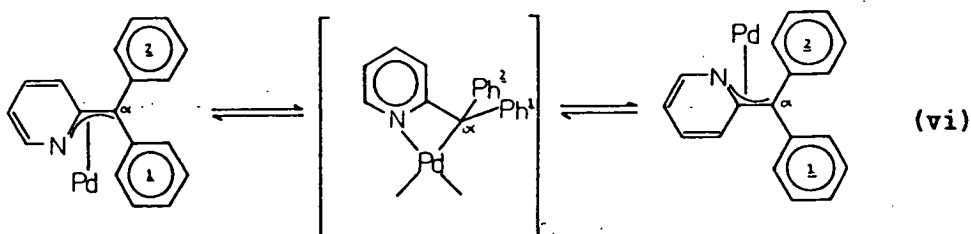


If η^3 -azaallylic bonding occurs, an analogous process to (iii) will not result in averaging of phenyl group environments as the two phenyl groups remain in chemically distinct environments after exchange, (v).



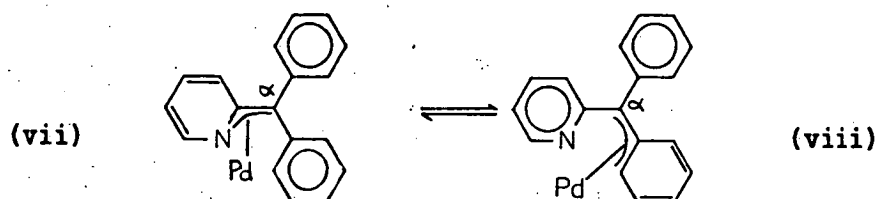
Additionally, the possibility of an allyl involving the pyridine C(3) atom would seem unlikely since this would involve palladium in bonding to the least electron rich site available to formation of an allylic bond. However, phenyl group equilibration may be possible via an alternative mechanism involving the transient

formation of a σ -bond in a four-membered ring, (iv), involving the nitrogen donor and C(α).



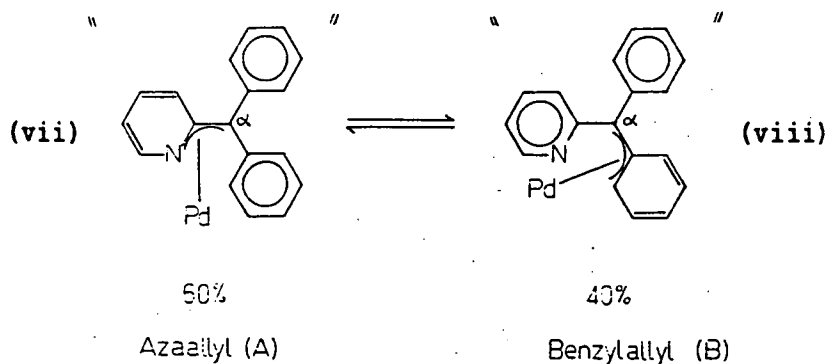
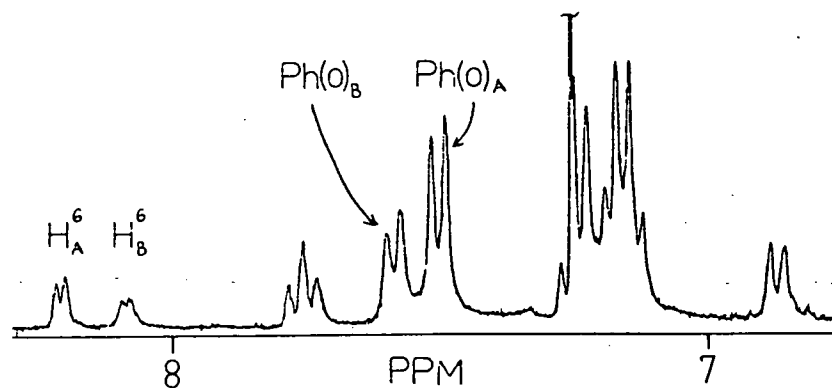
The existence of such an intermediate seems reasonable in view of the presence of a similar feature within the complex $[(\mu\text{-py-}M)(\text{py-}M)(\text{PhC-C})\text{PdCl}]_2$ discussed on page 140.

Metal shifts between azaallylic and benzylallylic bonding modes (vii \rightleftharpoons viii) may also be possible, in direct analogy to (ii).



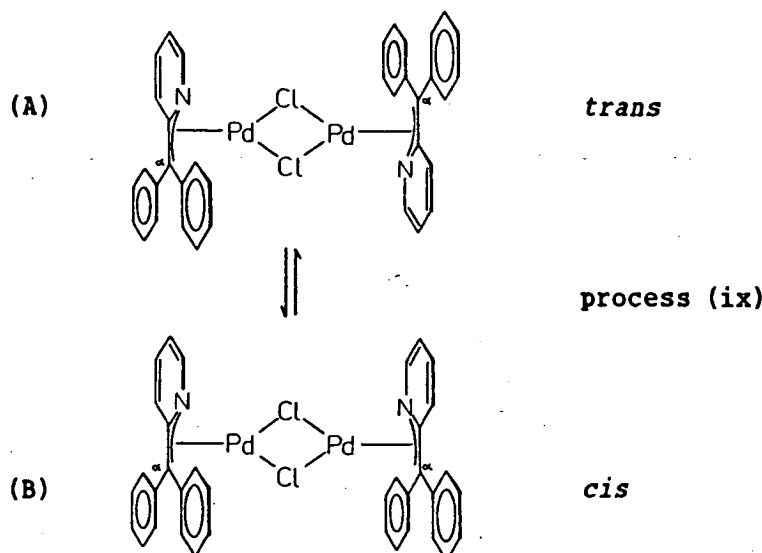
With the possibility of these processes occurring, several dynamic dimeric structures for $[(\text{pyPh}_2\text{C})\text{PdCl}]_2$ involving chlorobridging for the "isomers" in 3:2 ratio may be envisaged. For example, a dimer involving an equilibrium between η^3 -azaallylic and η^3 -benzylallylic bonding, or a dimer involving one of these bonding modes but with two geometric configurations of the ligand.

If an azaallyl / benzylallyl equilibrium is assumed (vii) \rightleftharpoons (viii), then a 3:2 isomer ratio would account for integration values observed in the ^1H nmr spectrum, where differences in chemical shift of pyridine H(6) and ortho-phenyl protons reflect the influence of two metal binding sites.



Thus, in this proposed equilibrium those environments directly affected by the site of metal binding give downfield signals, while those remote from the binding site appear upfield, approaching the resonance positions found in the free ligand. All signals are broadened at ambient temperature due to the rapid averaging processes (iii), (iv), and (vi), and η^3 -azaallylic bonding dominates the equilibrium due to the high electron density on the nitrogen atom.

The observed ^1H nmr features may also be explained in terms of the presence of one η^3 -allylic form in two geometric configurations. For example, if η^3 -azaallylic bonding is assumed for the reason stated above, a mixture of *cis* and *trans* isomers may contribute to give rise to slightly different ^1H nmr spectral patterns from intramolecular shielding effects.²⁹



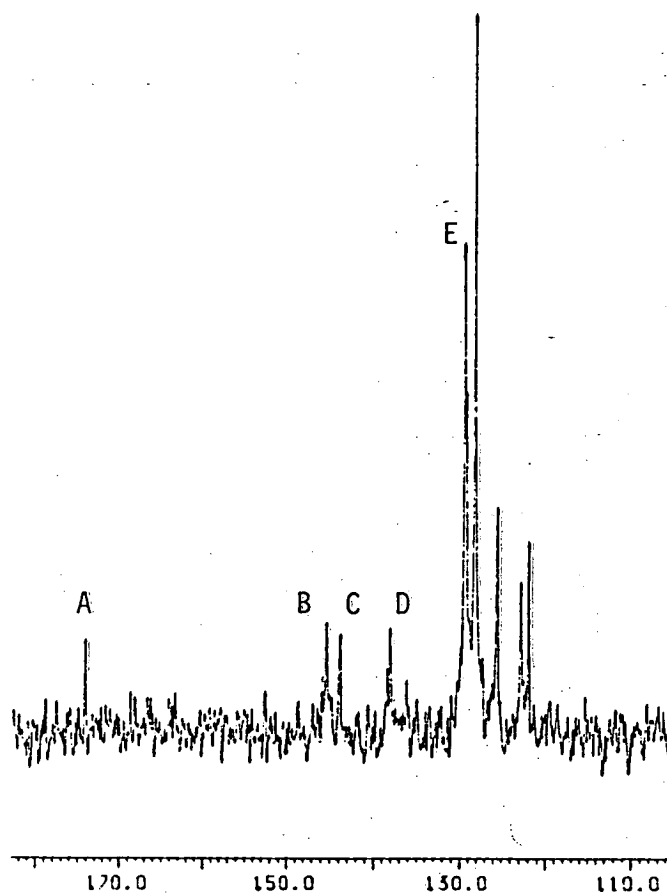
Using this interpretation exchange processes within the complex may also be similar to some of those previously described where, for example, phenyl ring equilibration occurs via formation of a four-membered σ -donor intermediate (page 136, process (vi)), and where free rotation of aromatic rings not involved in bonding is assumed.

In these terms, figure (A) above suggests that the downfield (shielded) pyridine H(6) resonance (page 137, H_A^6) arises from the *trans* form of the complex yielding a *trans* : *cis* ratio of ca. 3:2. Consistent with this interpretation, the *cis* isomer exhibits shielded ortho-phenyl resonance ($Ph(O)_B$) at ca. 7.58 ppm compared with ca. 7.51 ppm for ortho-phenyl resonance of the *trans* isomer ($Ph(O)_A$) also in 3:2 ratio, respectively.

Distinction between the two general interpretations is unclear on the basis of 1H nmr spectral evidence alone. However, the limited ^{13}C nmr data obtainable for the complex favours the latter interpretation.

The 1H decoupled ^{13}C nmr spectrum of the dimer at $-20^\circ C$ is shown below. The poor signal to noise ratio is a result of the low solubility of the complex. Resonances A-D arise from quaternary carbon atoms and E represents two signals of very similar chemical shift. Resonance A has been assigned to pyridine (C2) while resonances B and C have been tentatively assigned as

phenyl (C1) resonances (by comparison with related complexes shown on page 119, and 145). Resonance D has been tentatively assigned to C(α), the bridging carbon atom.



The ten line spectrum above is consistent with what would be expected for azaallyl or benzylallyl bonding alone, but not both, unless extensive accidental degeneracy occurs. Thus, ^{13}C data supports a process similar to (ix) (page 138) rather than (vii) \rightleftharpoons (viii) (page 137).

6.4 The Oxidative Addition of py_2PhCCl to Palladium(0)

In a similar manner to the reaction between pyPh_2CCl and $[(\text{dba})_2\text{Pd}]$, the ligand py_2PhCCl was reacted with $[(\text{dba})_2\text{Pd}]$. On passing the crude reaction product through a medium-pressure chromatographic column (silica gel, CHCl_3 elution) the complex was isolated as an intense magenta band (R_f 0.14) following a

yellow band of free dba (R_f 0.62).^{*} The eluent containing the complex was reduced to dryness under vacuum and the residue was recrystallised from dichloromethane/acetone. On standing, magenta crystals formed rapidly and a further crop was obtained by diethyl ether diffusion in a sealed chamber (39%). The complex is indefinitely stable under ambient conditions and is soluble in most common organic solvents. Microanalysis, I.R. and ^1H nmr spectra indicated the presence of both acetone and dichloromethane of solvation. Analytical values suggested a ratio L : Pd : acetone : dichloromethane of 1 : 1 : 0.3 : 0.3, and X-ray analysis on a crystal from the same preparation indicated a ratio 1 : 1 : 0.25 : 0.25. Over a few days the initially transparent crystals slowly become opaque, consistent with gradual loss of solvent molecules.

The complex has been characterised using I.R., nmr (^1H , COSY, ^{13}C , DEPT, ^{13}C - ^1H correlation¹⁷), and X-ray analysis.²⁸ As interpretation of nmr results is simplified by examination of the solid-state structure, this will be presented first.

6.4(i) The Solid State Structure of $[(\mu\text{-py-M})(\text{py-M})(\text{PhC-C})\{\text{PdCl}\}]_2 \cdot [(\text{CH}_3)_2\text{CO} \cdot \text{CH}_2\text{Cl}_2]_{0.5}$

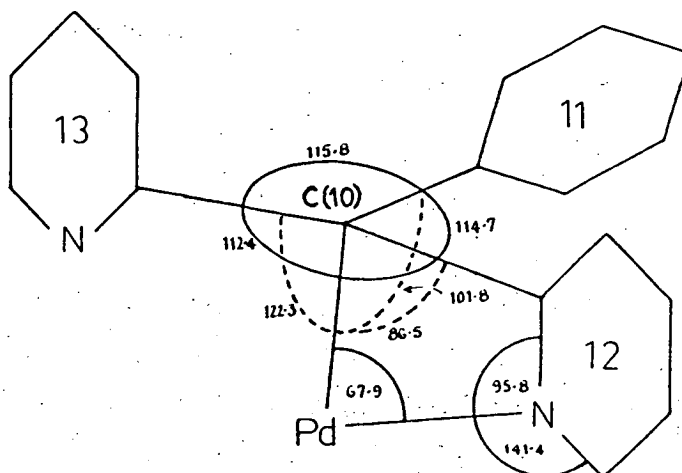
The title complex, obtained as deep magenta crystals from a dichloromethane/acetone solution (1:1) by ether diffusion in a sealed chamber, is composed of a dinuclear organometallic complex in association with molecules of acetone and dichloromethane of solvation. Each ligand, py_2PhC^- , is σ -bound to palladium, bridges between two palladium atoms with one donor group, and chelates to the supporting metal atom with the second donor group. The dimeric complex has minor differences in coordination geometry for the two palladium atoms (see Table 6.3 overleaf). Distorted square-planar geometry is based on a *trans* arrangement of nitrogen donors, one from the bridging moiety, and one from intramolecular coordination forming a four-membered ring (PdCCN).

* Use of alcohols e.g., MeOH, EtOH to increase solvent polarity should be avoided as these solvents cause rapid decomposition of the complex.

Bond angles about the palladium atoms range from $67.9(4)$ to $101.9(3)^\circ$ with the more acute angles resulting from the formation of four-membered chelate rings. The Pd...Pd separation of $2.855(2)\text{\AA}$ is somewhat smaller than that for the related 2-benzylpyridine complexes previously described on pages 116, and 129, with Pd...Pd distances $3.062(7)\text{\AA}$ and $3.184(3)\text{\AA}$, respectively.

The aromatic rings of the ligands are essentially planar with maximum deviation observed for C(2) of ring (23), 0.024\AA . Ring (12), chelating to Pd(1), forms a dihedral angle of 10.3° to the mean square plane defined by Pd(1)N₂C(Cl), and similarly, ring (22) forms a dihedral angle of 10.9° to Pd(2)N₂C(Cl). The pyridine rings bridging between the metal centers form a much larger dihedral angle, with ring (23) subtending an angle of 82.6° to the plane defined by Pd(1)N₂C(Cl) and ring (13) 83.9° to Pd(2)N₂C(Cl). The palladium atoms deviate from the projected mean planes of the coordinated aromatic rings. The minimum deviation is observed for Pd(2), 0.119\AA from ring (13), and the maximum, 0.379\AA , for Pd(2) from ring (22).

Quaternary carbon atoms bonded to palladium show substantial distortion toward planarity, and angles about C(10) (bound to Pd(1)) range from $86.5(6)$ to $122.3(7)^\circ$, and similar distortion is found about C(20). Selected angles about C(10) and the near environment are shown below. The average distance between bonded quaternary carbon atoms is $1.51(2)\text{\AA}$, typical of carbon-carbon single bonds.²³ Thus, the distortion about C(10) and C(20) results from steric constraint rather than a change in bond order about these atoms.



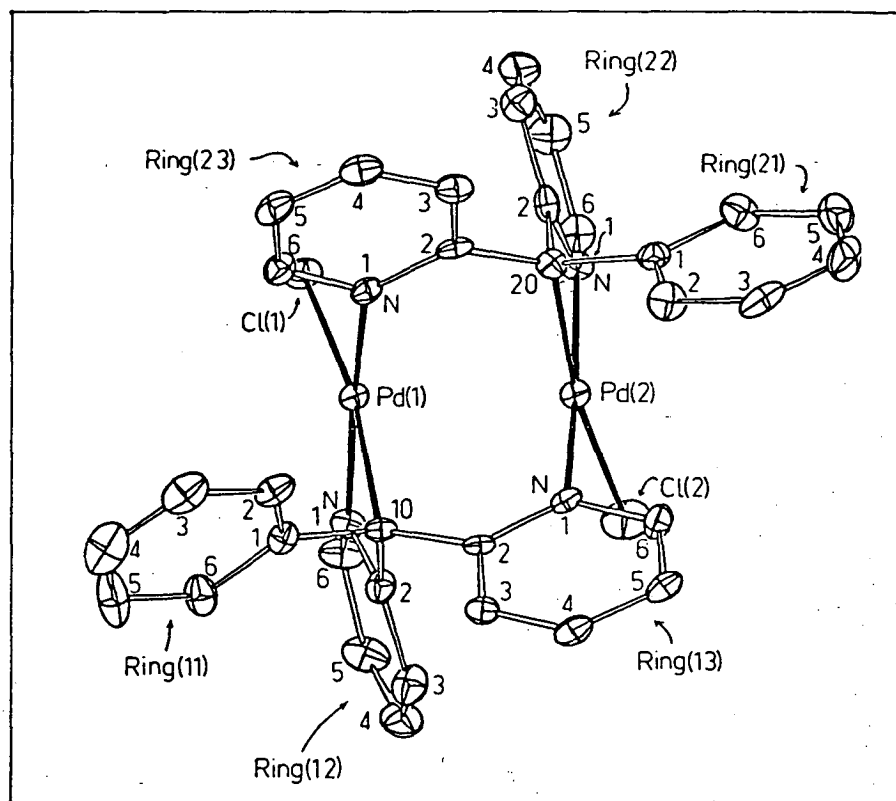
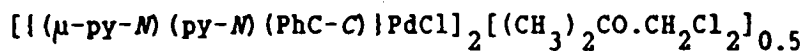
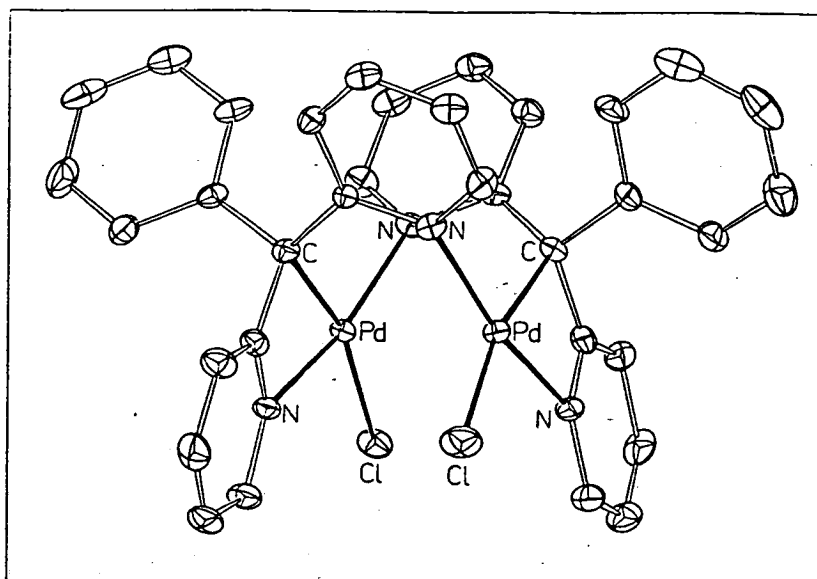


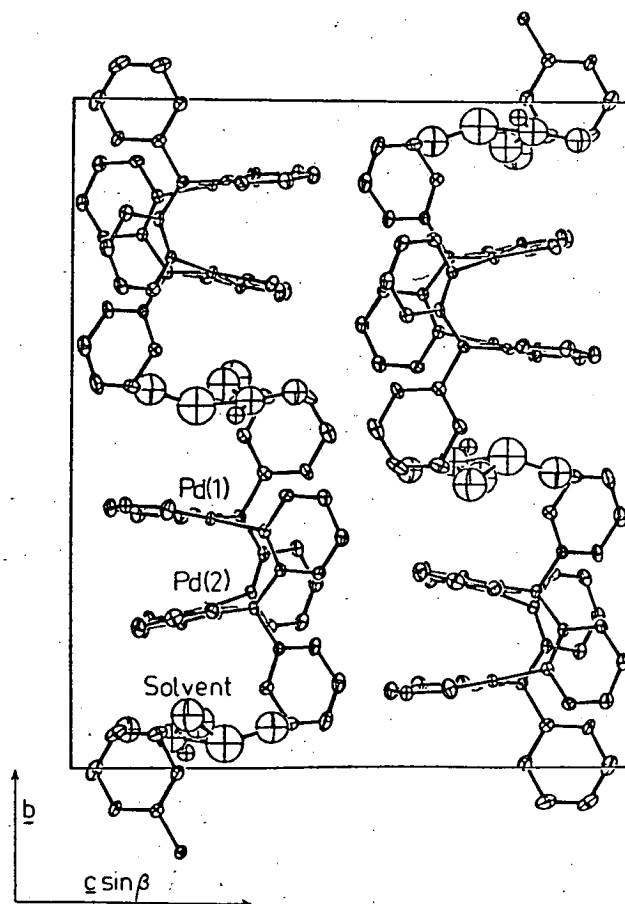
Table 6.3 Palladium environments.

Atoms	n = 1	n = 2
Distances (Å)		
Pd(n) - Cl(n)	2.384(3)	2.377(5)
Pd(n) - C(n0)	2.101(9)	2.091(13)
Pd(n) - N(n22)	2.005(11)	2.012(8)
Pd(n) - N(n'32)	2.058(10)	2.047(7)
Pd(1) ... Pd(2)	2.855(2)	
Angles (degrees)		
Cl(n) - Pd(n) - C(n0)	166.3(3)	168.0(3)
Cl(n) - Pd(n) - N(n22)	99.8(2)	101.9(3)
Cl(n) - Pd(n) - N(n'32)	93.8(2)	92.1(3)
C(n0) - Pd(n) - N(n22)	67.9(4)	68.4(4)
C(n0) - Pd(n) - N(n'32)	98.5(4)	97.6(4)
N(n22) - Pd(n) - N(n'32)	166.3(3)	165.9(4)

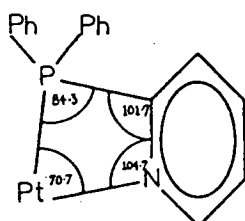
An alternative view of the dimer emphasising the $\overline{\text{PdNCC}}$
four-membered ring.



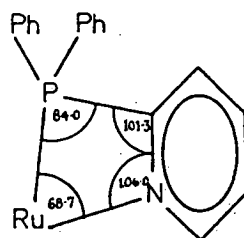
Unit Cell contents showing disposition of solvent molecules
(acetone and dichloromethane).



Although no other complexes possessing a $\overline{\text{PdNCC}}$ four-membered ring have been structurally characterised, some complexes containing a $\overline{\text{MNCP}}$ ring involving the ligand pyPh_2P have been the subject of crystallographic analysis.^{24,25} Bond angles in the planes of the four-membered chelate rings of some representative complexes are shown below.



from $[(\text{pyPh}_2\text{P})_2\text{PtCl}]^+$
(Ref. 24)

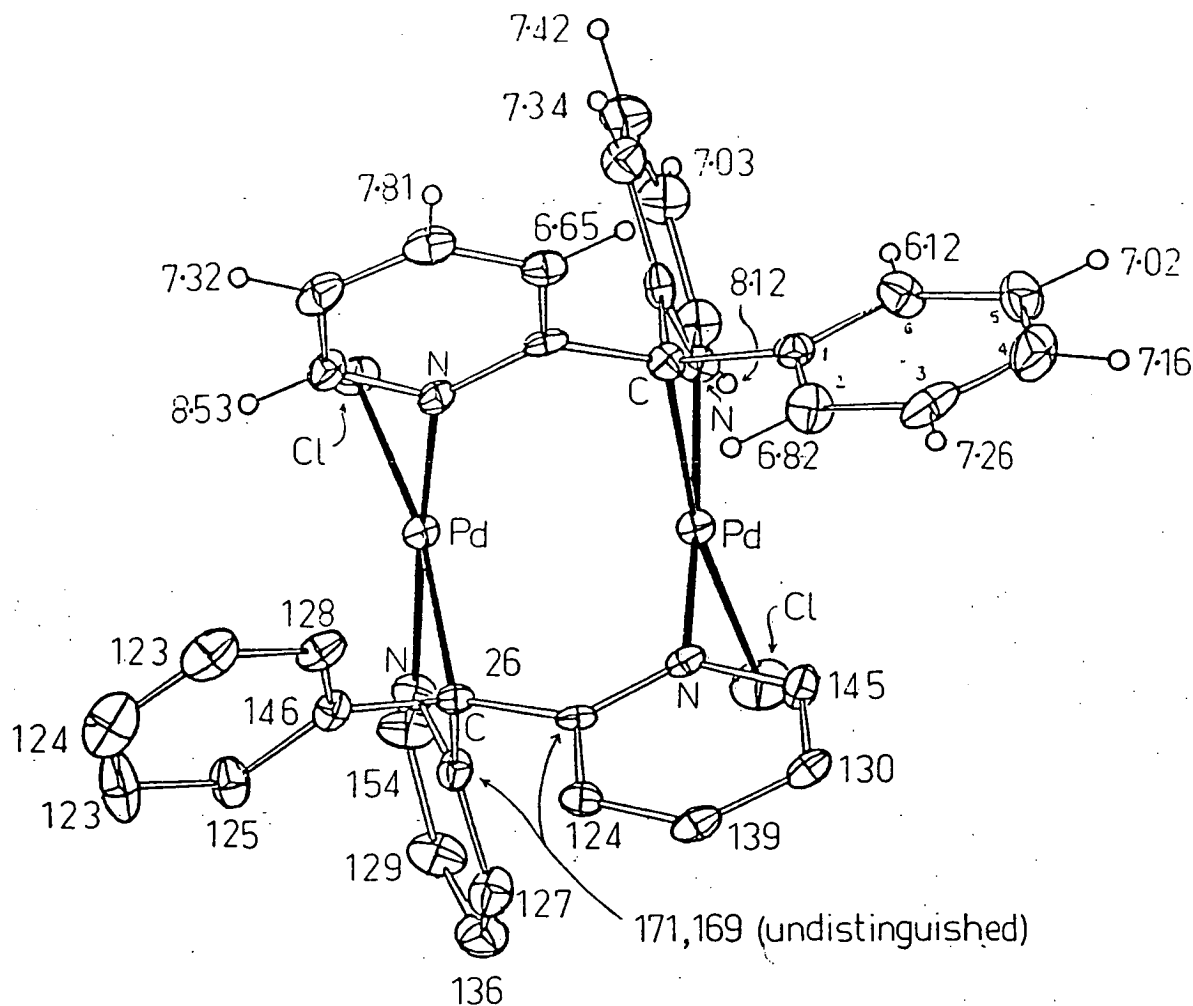


from $[(\text{pyPh}_2\text{P})\text{Ru}(\text{CO})_2\text{Cl}_2]$
(Ref. 25)

The deprotonated α -picolyl group $\text{py}(\text{Me}_3\text{Si})\text{HC}^-$ also forms a four membered chelate ring to zirconium but, in the solid state, bonding of the ligand appears to be intermediate between a chelate structure and an η^3 -azaallyl structure.²⁶

6.4(ii) Nmr Characterisation

Standard high resolution ^1H nmr spectroscopy, in conjunction with COSY spectroscopy, allows identification of three J-coupled subgroups (i.e. three aromatic ring environments) in the aromatic resonances associated with the dimer. Two H(6) resonances are readily identified in the downfield region of the ^1H nmr spectrum, overleaf, with the furthest downfield resonance being assigned to H(6) environments of the bridging aromatic rings by the expected deshielding effects of the metal centers (subsequently supported by the H(3) resonance positions derived from the COSY spectrum). Thus, all proton resonances may be assigned as shown below.

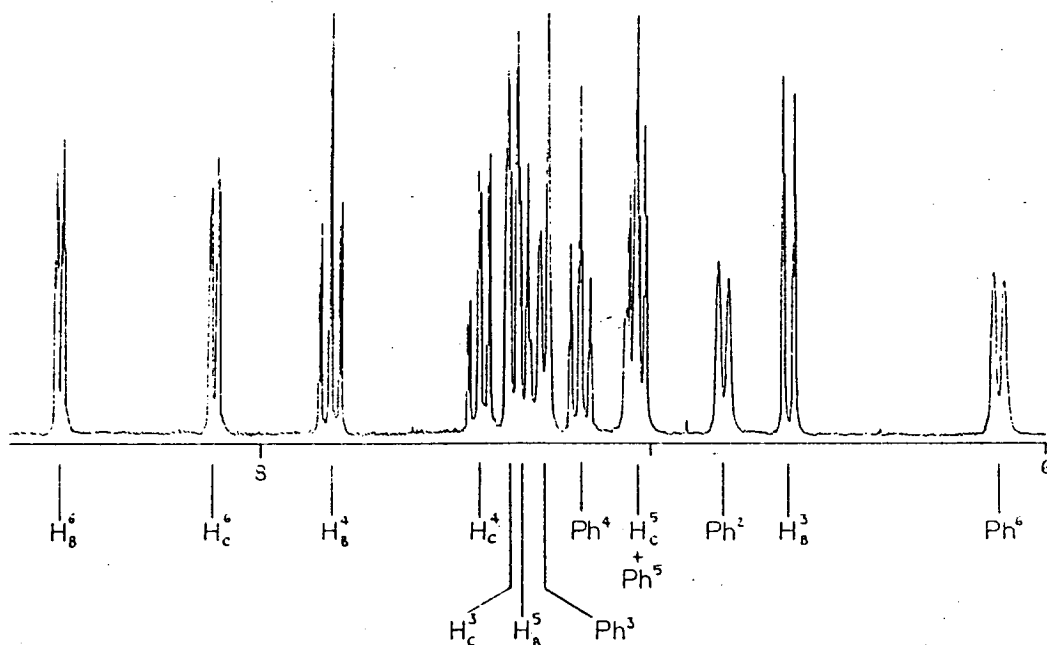


¹H (upper) and ¹³C (lower) Chemical Shift Positions

The resonance position of H(3) on the bridging pyridine group at 6.65 ppm (H_B^3), compared with 7.34 ppm for the chelating donor (H_C^3), indicates shielding of the former by the attached phenyl substituent. The association of this H(3) proton with the most downfield H(6) resonance at 8.53 ppm (H_B^6) supports the assignment of the latter.

All resonances associated with the phenyl ring are clearly separated, presumably as a result of hindered rotation of the substituent. Thus, the proton closest to the chelating pyridine ring has been assigned to the most upfield resonance at 6.12 ppm (Ph^6), and the others have been assigned in relation to this, in

conjunction with their splitting pattern.

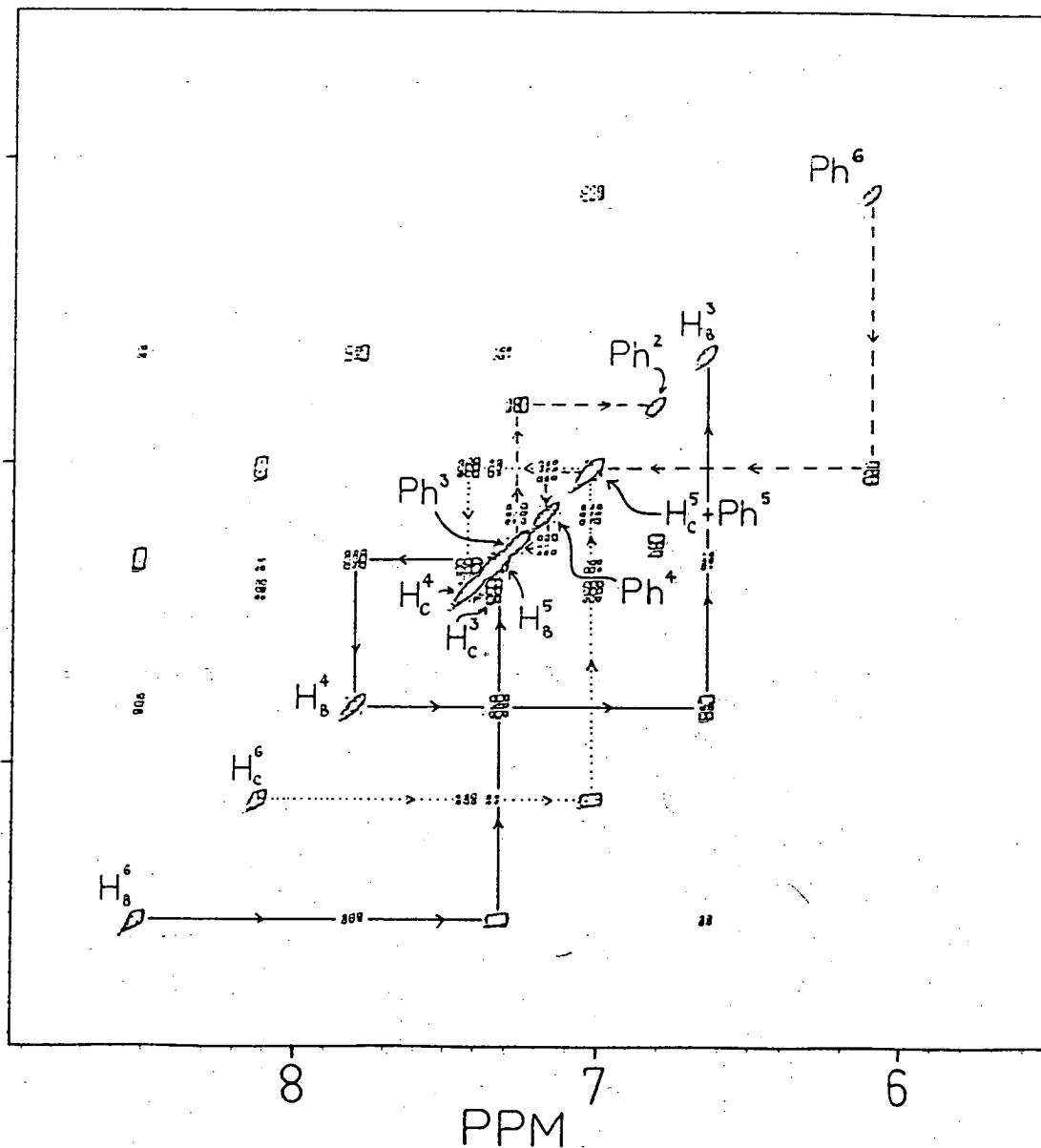


N.B. Subscript B indicates bridging pyridine ring and
Subscript C indicates chelating pyridine ring.

For atom numbering on the phenyl substituent see page 145.

The ^{13}C nmr spectrum (^1H decoupled) of the dimer shows the expected sixteen resonances for aromatic carbon atoms as well as one resonance at 25.88 ppm for the bridgehead carbon atom. Using a DEPT sequence three aromatic quaternary carbon atoms have been identified resonating at 171.31, 168.54 and 146.00 ppm. From the expected similarity in chemical shift values the former two resonances have been assigned as C(2) atoms of the pyridine rings, although individual assignment is uncertain. The resonance at 146.00 ppm has been assigned to C(1) of the phenyl substituent. As all proton environments have been identified other non-quaternary ^{13}C resonances have been deduced using ^{13}C - ^1H correlation spectroscopy yielding the assignments on page 145.

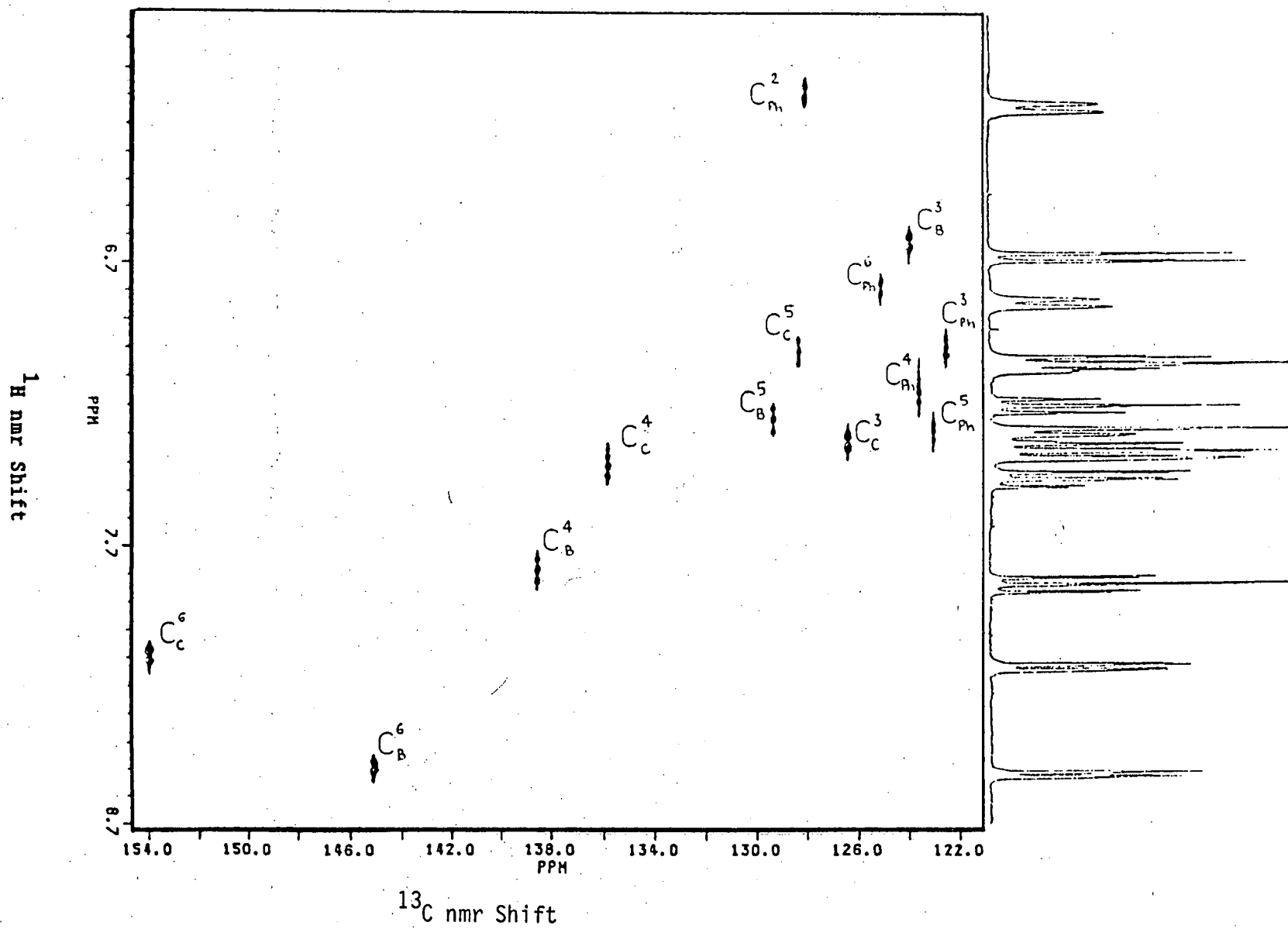
The COSY spectrum of $[(\mu\text{-py-M})(\text{py-M})(\text{PhC-C})\text{PdCl}]_2$
 $[(\text{CH}_3)_2\text{CO} \cdot \text{CH}_2\text{Cl}_2]_{0.5}$
 (Aromatic Region)



- _____ Connectivity in bridging pyridine ring (subscript B)
 Connectivity in chelating pyridine ring (subscript C)
 - - - - - Connectivity in phenyl ring

See page 145 for atom numbering.

$^{13}\text{C} - ^1\text{H}$ Correlation Spectrum



6.5 Attempted Oxidative Addition of py_3CCl to Palladium(0)

In a similar manner to the reaction of the other triarylmethylchloride reagents with $[(\text{dba})_2\text{Pd}]$, py_3CCl was reacted in benzene with $[(\text{dba})_2\text{Pd}]$. After 20h the solution was filtered free of insoluble material and the filtrate was separated as previously described. By these means some free dba and traces of ligand as well as $[(\text{dba})_3(\text{CHCl}_3)\text{Pd}_2]$ were recovered from the filtrate, but no palladium(II) complex of the ligand was isolated. The sparingly soluble brown solid removed prior to chromatographic separation showed the presence of ligand and dba, from I.R., and palladium, by ignition of a small sample. The solid is presumed to be a palladium(0) complex of the ligand, possibly polymeric. A similar monomeric Pd(0) complex of bpy, $[(\text{bpy})(\text{dba})\text{Pd}]$, has been isolated and structurally characterised.²⁷

6.6 Conclusions

The reaction between $\text{pyPhHC}^-\text{Li}^+$ and $\text{trans}-[(\chi\text{-pic})_2\text{PdCl}_2]$ gives diverse reaction products. The reaction products represent the result of direct reaction between lithio-ligand and palladium substrate, as well as products from donor exchange, decomposition, and reaction with solvent. Interconversion of some of the organometallic complexes by donor exchange is possible under appropriate conditions.

Oxidative addition of pyPh_2CCl to $[(\text{dba})_2\text{Pd}]$ gives a dinuclear complex, $[(\text{pyPh}_2\text{C})\text{PdCl}]_2$, where the ligand is allylically bound to palladium. Exchange processes observed in the molecule have been attributed to either an equilibrium mixture of azaallylic and benzylallylic bonding or *cis* and *trans* isomers of a single allylic form, where other processes including a transient σ -bound species may be involved in the fluxional process(es).

A similar reaction between py_2PhCCl and $[(\text{dba})_2\text{Pd}]$ has resulted in isolation of a dimeric organopalladium chloride complex containing a Pd-C σ -bond, involving formation of a four-membered PdNCC palladocycle.

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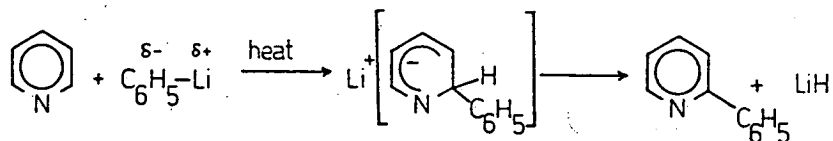
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CHAPTER SEVEN

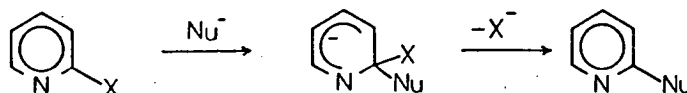
LIGAND SYNTHESIS

7.1 Pyridine and its Effects on Ring Substituents

Replacement of one CH group in benzene by a nitrogen atom, to give pyridine, results in a marked change in reactivity of the remaining CH groups. Molecular orbital calculations show that the π -electron density at position 3 of the pyridine ring is higher than that at positions 2 or 4.¹ This is a consequence of nitrogen being more electronegative than carbon. Thus, although pyridine ring carbon atoms undergo electrophilic substitution reactions under vigorous conditions, their chemistry is usually dominated by nucleophilic substitution reactions, particularly at the 2, 4 and 6 positions.² The reactivity of pyridine toward nucleophilic substitution is so great that even the powerfully basic hydride ion may be displaced,³ for example, on reaction with phenyllithium.



Pyridines bearing halogen substituents in the 2 and/or 6 positions are more susceptible to nucleophilic substitution than the related halobenzenes. In general, these reactions involve loss of halogen via an addition-elimination sequence where the nucleophile adds to the halogen bearing carbon atom, followed by elimination of halide.⁴

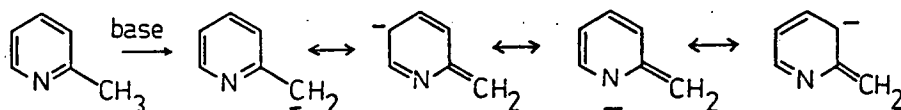


* Some new ligand syntheses appear in Publications 1,3,4, and 6, pages 220, 224, 228, and 240, respectively.

Thus, for example, 2-bromopyridine pyridylates the stabilised carbanions of diethylethylmalonate⁵, and more importantly to this work, of 2,2'-bipyridylmethane⁶ (see page 156).

Lithiopyridine reagents are not formed by interaction of halopyridines with lithium metal but by halogen-metal exchange with an alkyl- or aryllithium, usually n-butyllithium. The most frequently encountered lithiopyridine reagents of this type have lithium residing at the 2 or 4 positions, although all isomeric forms are known. The reagents undergo a wide range of reactions with, for example, aldehydes, ketones and esters and this subject has been reviewed.⁷ In particular, organic molecules derived from 2-lithiopyridine have found extensive use as ligands for inorganic chemistry.⁸

The effect of the nitrogen atom is not limited to the aromatic ring. A strong base such as butyllithium or potassium amide will quantitatively deprotonate the α -carbon substituent in, for example, α -picoline (2-methylpyridine)⁹. However, for deprotonation of the methyl substituent in its carbocyclic analogue, toluene, more basic reagents are required, for example, butyllithium in the presence of triethylenediamine¹⁰. For α -picoline, charge may be favourably localised on the ring nitrogen, a situation unavailable to the benzene nucleus which typically serves as a source of electrons for electrophilic reagents.

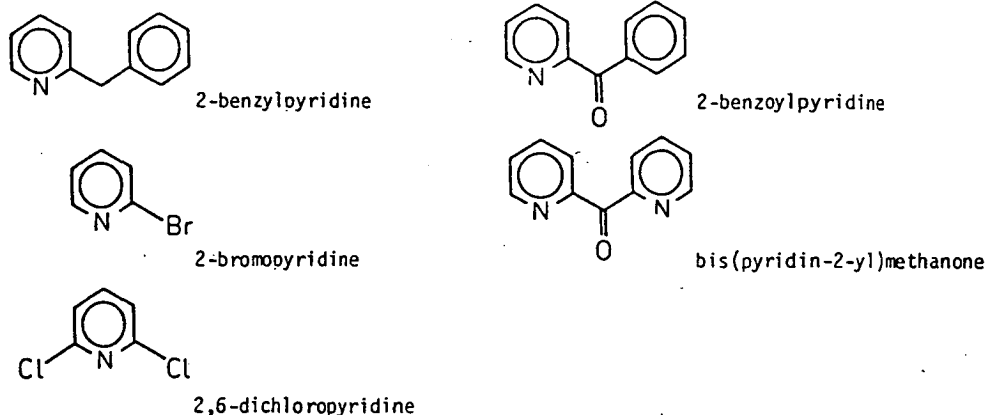


Similar structures to those above may be drawn for the analogous 4-substituted pyridine, but not for the system containing a 3-substituent.

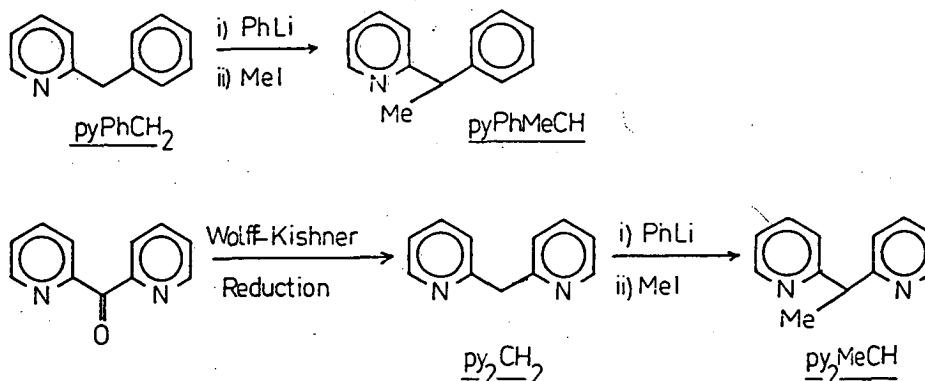
7.2 Starting Materials

The pyridine containing starting materials used for this study are listed below and are readily available from commercial sources. Both 2-benzylpyridine and bis(pyridin-2-yl)methane (from

Wolff-Kishner reduction of bis(pyridin-2-yl)methanone¹¹, or their derivatives, have been used as sources of carbanions for nucleophilic attack on the halopyridines below. Similarly, 2-lithiopyridine and phenyllithium have been used as anion sources for addition to the ketones listed.



Some transformations of 2-benzylpyridine and bis(pyridin-2-yl)methanone have been necessary for the proposed syntheses, and these are shown below.



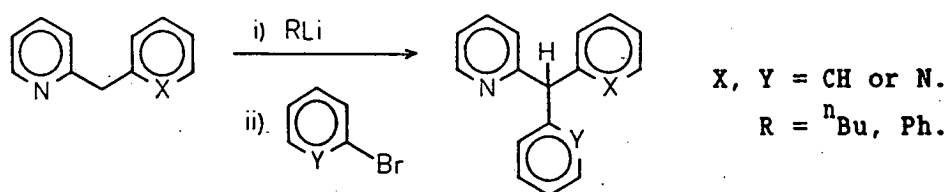
(Experimental, page 209 and 211)

7.3 Ligands Containing One Bridging Carbon Atom:

"Simple Ligands"

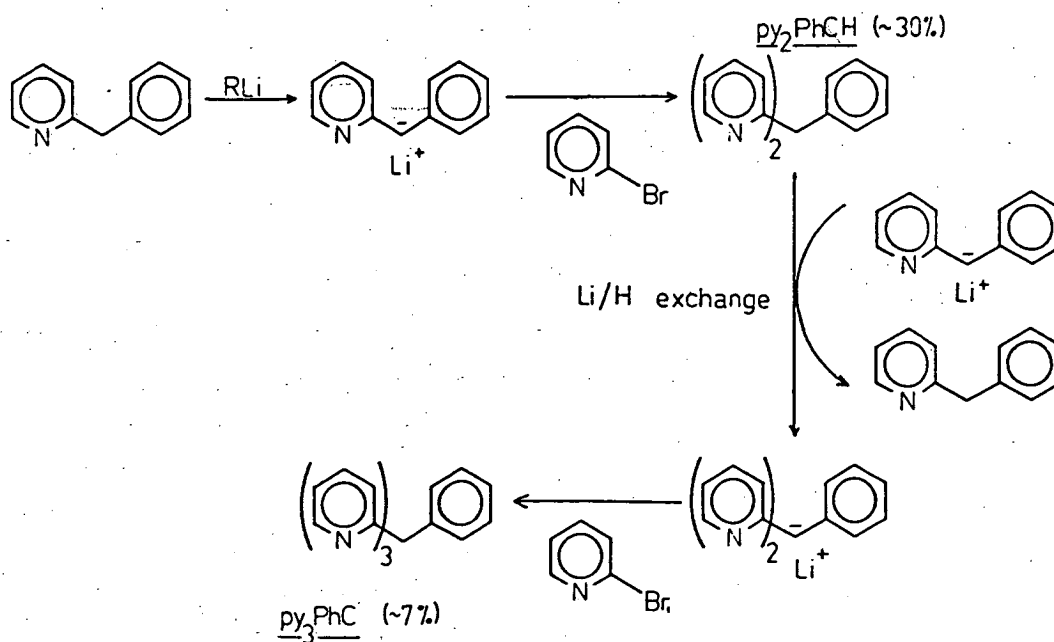
For the purpose of studying the coordination chemistry of Pd(II) with simple pyridine N-donor ligands, two types of triarylmethyl ligands have been required, $\text{py}_n\text{Ph}_{3-n}\text{CH}$ and $\text{py}_n\text{Ph}_{3-n}\text{CCl}$, where $n = 1-3$.

The methane series, $\text{py}_n\text{Ph}_{3-n}\text{CH}$, have all been previously reported^{6,12} and may be prepared according to the general equation below.



(Experimental page 205)

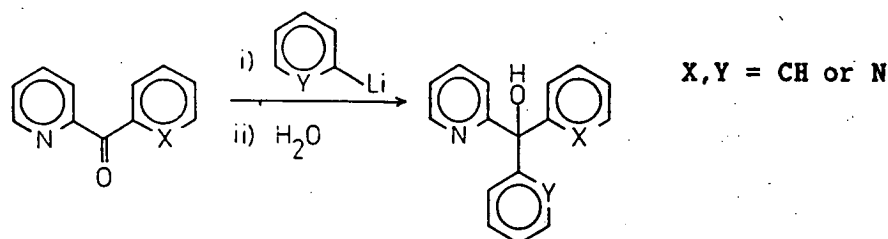
The member pyPh_2CH is commercially available (Aldrich) and the others may be prepared in moderate yield (ca. 30-60%). A byproduct of the synthesis of py_2PhCH has also been of use as a new tripodal ligand, and presumably arises as a result of lithium-hydrogen exchange during reaction (see Experimental page 205).



The exchange reaction is not readily controlled without blocking one of the methylene hydrogen sites in the starting material (with, for example, a more chemically inert methyl group), and this exchange presumably contributes to the low yield in preparation of some ligands.

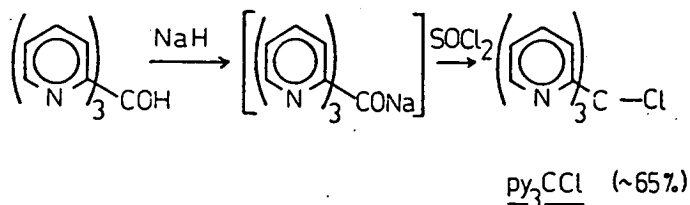
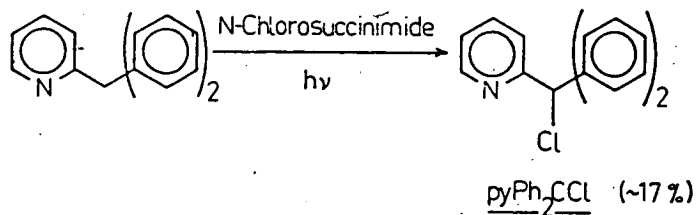
In the analogous reaction producing py_3CH no byproduct of the form py_4C has been isolated or detected. This may reflect differing anion stabilities.

The chloromethane ligands $\text{py}_n\text{Ph}_{3-n}\text{CCl}$ have all been prepared by chlorination of the analogous methanols, $\text{py}_n\text{Ph}_{3-n}\text{COH}$. The methanols are prepared from the ketones 2-benzoylpyridine and bis(pyridin-2-yl)methanone according to the general equation,



(Experimental page 207)

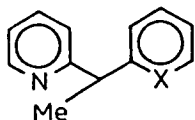
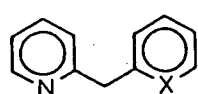
Of the chloromethanes (Experimental page 208) two members have been previously reported, pyPh_2CCl from free radical chlorination of pyPh_2CH ,¹⁴ and py_3CCl from reaction of the corresponding methanol with NaH and SOCl_2 .¹⁵



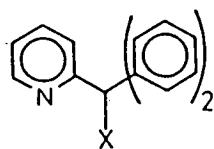
As the latter method suggested superior yields, it was adopted for the synthesis of all chloromethane ligands. Thus, the new member py_2PhCCl has been prepared in 67% yield and pyPh_2CCl has

been prepared, using a slight modification to the method, in up to 56% yield. The latter chloromethane is readily hydrolysed by water, regenerating the alcohol, and thus is similar to triphenylmethylchloride in hydrolytic sensitivity. As ^1H nmr reference compounds for the extended ligand systems (see page 41), the ethane series $\text{py}_n\text{Ph}_{3-n}\text{CMe}$, have been prepared from their respective methane precursors by reaction with methyllithium and methyl iodide (see Experimental page 206). For $n = 2, 3$ crystalline solids were obtained and fully characterised. However, for $n = 1$ the product was obtained as a very viscous oil and characterisation was limited to ^1H nmr and M.S. in this case.

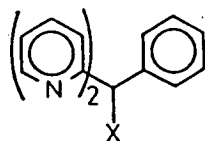
A summary of the simple ligands prepared and including those commercially available is shown below.



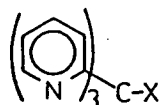
$\text{X} = \text{CH or N}$



$\text{X} = \text{H, OH, Me}^*, \text{Cl}^{**}$



$\text{X} = \text{H, OH, Me}^*, \text{Cl}^*$



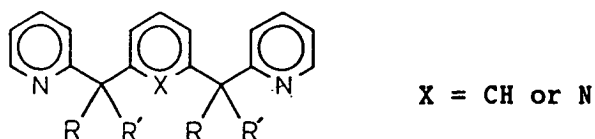
$\text{X} = \text{H, OH, Me}^*, \text{Cl, Ph}^*$

* new compounds

** improved method

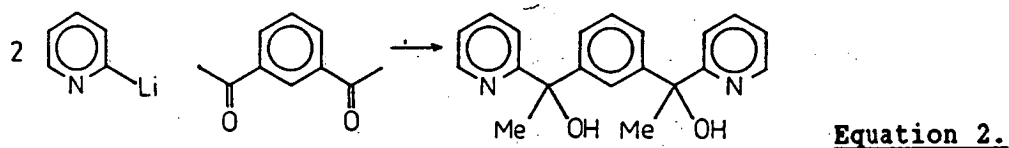
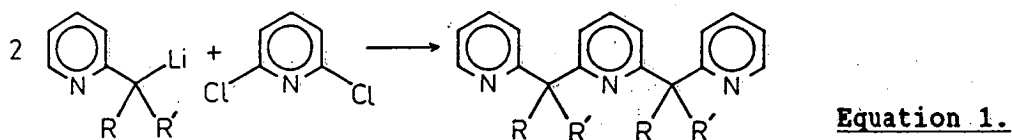
7.4 Ligands Containing Two Bridging Carbon Atoms: "Extended Ligands"

To further extend the study of coordination properties of Pd(II) with ligands related to those above, new ligands containing the structural unit below were desired.



As these structural units possess symmetry about the central aromatic ring the starting materials 2,6-dichloropyridine, 1,3-diacetylbenzene, and dimethylisophthalate have been employed.

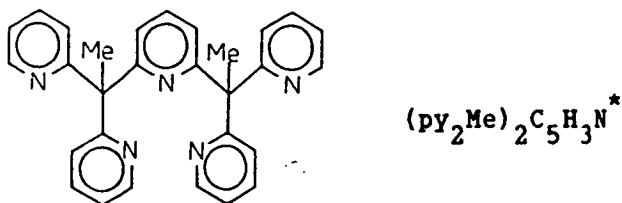
Two general reaction types were envisaged for the formation of the basic structural skeletons and these are generalised in equations 1 and 2.



To avoid the deleterious effects of lithium/hydrogen exchange previously mentioned, the substituted pyridine starting materials in Equation 1 were limited to those that contained only one site for deprotonation, i.e., pyPhMeCH and py₂MeCH.

7.4(i) Extended Ligands Linked by a Pyridine Nucleus.

Closely related to the simple ligand py_3CH , the ligand below was synthesised according to Equation 1, where $\text{R} = \text{Me}$ and $\text{R}' = \text{pyridin-2-yl}$ (see Experimental page 209).

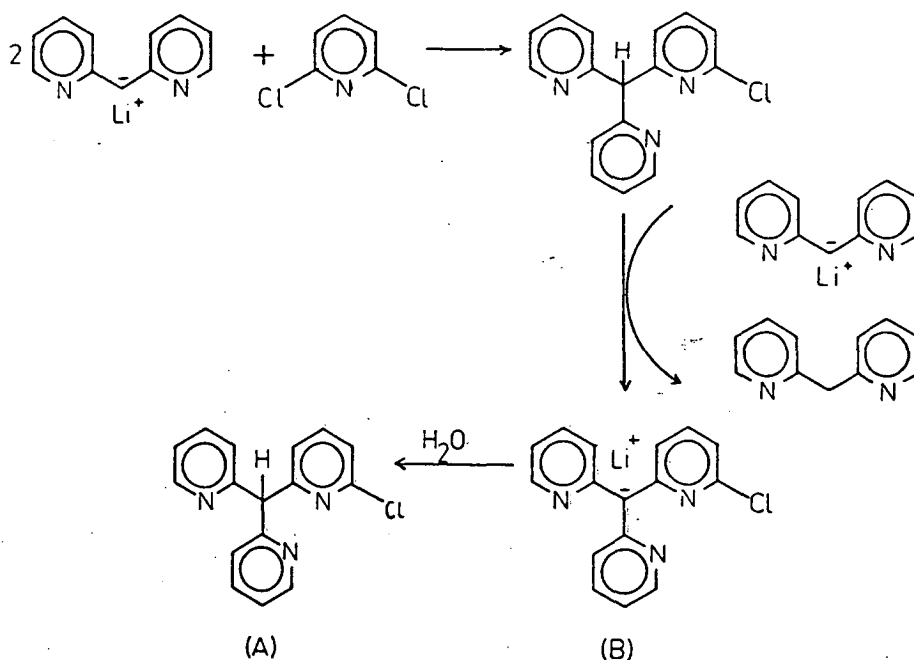


As a potentially ~~pentadentate~~ ligand possessing N-donors that may all form mutually normal M-N bonds when coordinated to a metal ion, the ligand may have application to transition metals that commonly adopt octahedral geometry as well as for investigation of extension of the coordination sphere of metals that generally adopt square-planar geometry.

The ligand is produced in fairly low yield (ca. 40%) but is readily isolated as a highly crystalline colourless solid. Observation of the reaction and analysis of the products suggests that monosubstitution of the 2,6-dichloropyridine is a fairly rapid process while addition of the second substituent is much slower. After hydrolysis and isolation of the desired product, analysis of the residue shows the presence of substantial quantities of the monosubstitution product and py_2MeCH (from ^1H nmr and M.S.).

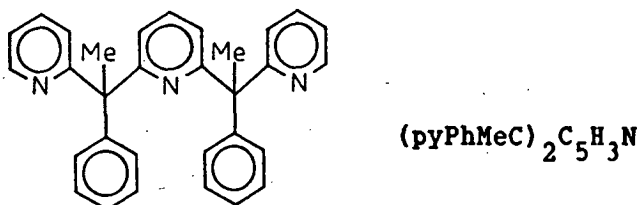
A reaction between lithiated py_2CH_2 with 2,6-dichloropyridine in 2:1 mole ratio under similar conditions, as a possible route to the non-methylated analogue of $(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}$, gave only the monosubstitution product (A) (^1H nmr, M.S.) as a viscous oil, indicating that lithium-hydrogen exchange may terminate the reaction after formation of the salt (B).

* Potential bonding modes to Pd(II) are shown on page 7.



The ligand $(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}$ shows the expected physical and spectral characteristics, with the pyridine H(6) and methyl protons being the most readily identifiable environments in the ^1H nmr spectrum. The ^1H nmr spectrum of the palladium(II) acetate complex of this ligand allows a near complete assignment of ligand proton resonances when coordinated (see page 38).

The extended ligand related to py_2PhCH , shown below, has been prepared under similar conditions (see Experimental page 211).



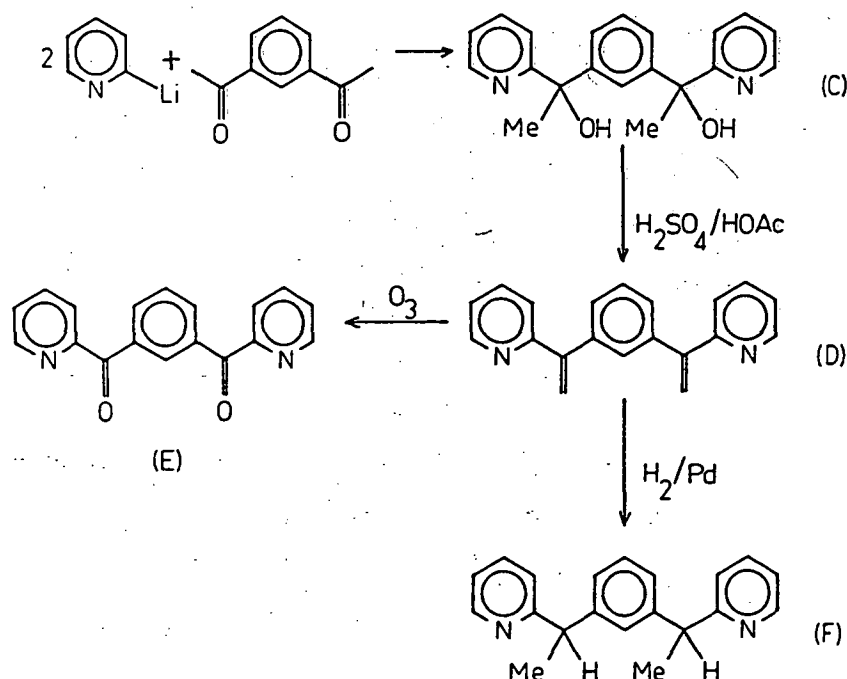
The ligand is formed in low yield (ca. 30%) as a highly crystalline colourless solid and is composed of a mixture of *meso* and *racemic* diastereoisomers. Separation of the diastereoisomers is described elsewhere (see page 90). The *meso* and *racemic*

diastereoisomers have similar ^1H nmr spectral characteristics, and thus, the proportions of each isomer present in the ligand mixture could not be determined by this method due to overlap of resonances.

Apart from the usual methods of characterisation, the identity of the *meso* form of the ligand has been established by X-ray crystallography of its complex with methylmercury(II) nitrate (page 89) and palladium(II) acetate (page 30). These structural studies show two bonding modes of the ligand, tripodal tridentate and planar-tridentate, respectively.

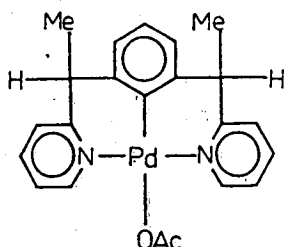
7.4(ii) Extended Ligands Linked by a Benzene Nucleus

For investigation of cyclometallation reactions of Pd(II) with extended ligands, those linked by a central benzene nucleus similar to that in Equation 2 (page 159) have been sought. Due to the interesting coordination properties of the ligand $(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}$, containing chiral bridging groups, the benzene linked ligand (F) was prepared according to the scheme below (see Experimental page 213).



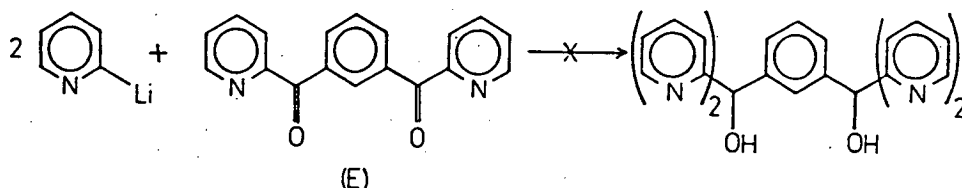
Compounds (C) and (D) were not isolated in a pure state. However, a highly crystalline derivative (E) of the alkene (D) has been prepared by ozonolysis¹⁶, and the desired product (F) may be purified by distillation to give a near colourless viscous oil. The diketone (E) has been fully characterised and, although microanalysis of (F) has not been attempted due to the nature of the liquid, a satisfactory analysis of a cyclopalladated derivative of it has been obtained (see Experimental page 214 and page 188). Solid state structural studies of complexes containing (E) and (F) shown on pages 79 and 75, respectively, have confirmed the ligand structures.

The ¹H nmr spectrum of (F) also confirms the structure given but has not allowed the proportions of diastereoisomers to be ascertained. Its cyclometallation product, below, has been shown to contain *meso* and *racemic* forms of the ligand.

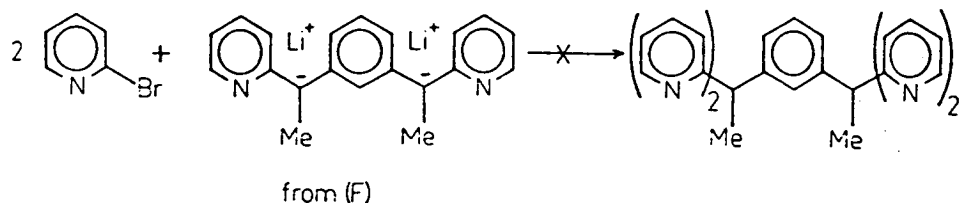


The details of the ¹H nmr spectrum of this complex are discussed elsewhere (see page 63).

Attempts to use both (E) and (F) as precursors to form benzene linked ligands, similar to those obtained using 2,6-disubstituted pyridines (Equation 1, page 159), were not successful.



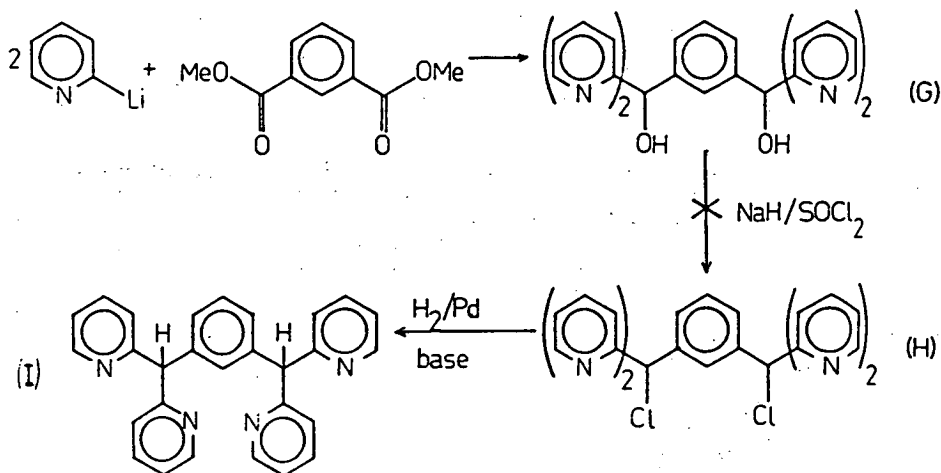
Equation 3.

Equation 4.

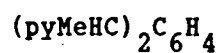
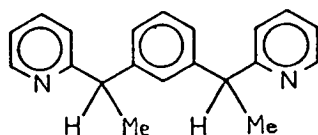
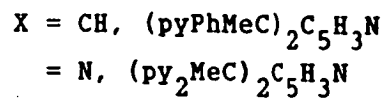
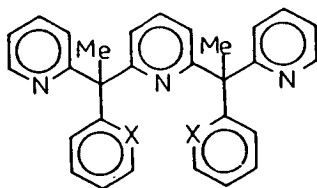
Following a similar procedure to that described for preparation of py_3COH (see ref, 13), the reaction given in Equation 3 was severely hampered by the insolubility of the ketone (E) in either diethyl ether or tetrahydrofuran at the low temperatures necessary for the stability of 2-lithiopyridine (ca. -30°C , or below).

The reaction described in Equation 4, conducted in a similar manner to the preparation of py_3CH or py_2PhCH (see Experimental page 205), produced only tarry material, presumably resulting from lithium-halogen exchange and subsequent decomposition of the lithiopyridine.

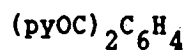
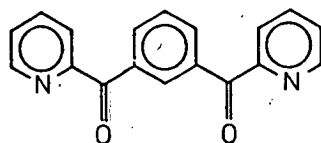
As an alternative synthetic method to Equations 3 and 4, reaction between 2-lithiopyridine and dimethylisophthalate has produced the alcohol (G) in low yield (36%). Attempted chlorination by the method previously described to give (H) was unsuccessful, presumably in part due to the very low solubility of (G). Attempts to reduce (G) directly to (I) have been unsuccessful to date.



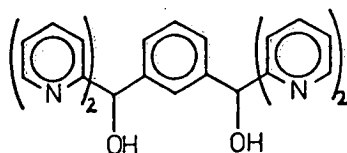
A summary of the new extended ligands is given below.



Fully characterised precursors and derivatives include,



and



1. Miller, R.L., Lykos, P.G., and Schmeising, H.N.
J. Am. Chem. Soc., 1962, 84, 4623.
2. For example, see
Boulton, A.J. and McKillop, A.
"Reactivity of Six Membered Rings" in
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A.R., and Rees, C.W., (Eds), Pergamon Press, Oxford,
1984, 2, 29.
3. Evans, J.C.W., and Allen, C.F.H.
Org. Synth., 1956, Coll. Vol. II, 517.
For comment on the intermediate structure see
Fraenkel, G., and Cooper, J.W.,
Tetrahedron Lett., 1968, 1825.
4. For example, see
Uff, B.C.
"Pyridines and their Benzo Derivatives: (iii)
Reactivity of Substituents", in "Comprehensive
Heterocyclic Chemistry", Katritzky, A.R., and Rees,
C.W., (Eds), Pergamon Press, Oxford, 1984, 2, 359.
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J. Am. Chem. Soc., 1935, 57, 1891.
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Hayhurst, G.
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7. Yale, H.L.
Chem. Heterocycl. Compd., 1974, 14, Suppl. 2, 489.
8. For example, see
Parks, J.E., Wagner, B.E., and Holm, R.H.
J. Organomet. Chem., 1973, 56, 53.
and for an exhaustive compilation see,

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"Pyridine and its Derivatives", Newkome, G.R. (Ed.), John
Wiley and Sons, New York, 1984.

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Eaborn, C., and Shaw, R.A.
J. Chem. Soc., 1955, 3306.
Osuch, C., and Levine, R.
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Inorg. Chem., 1981, 20, 4293.
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Otto, P.Ph.H.L.
Recueil, 1951, 1054.
14. Markgraf, J.H., Berryhill, S.R., Groden, L.R., Hensley,
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J. Org. Chem. 1975, 40(4), 417.
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Pappas, J.J., and Keaveney, W.P.
Tetrahedron Lett., 1966, 4273.
Also see,
Kuczkowski, R.L.
Acc. Chem. Res., 1983, 16, 42.

CHAPTER EIGHT

EXPERIMENTAL

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne, or the Canadian Microanalytical Service, Vancouver, on samples dried over P_2O_5 at room temperature *in vacuo* unless otherwise stated. Melting points were determined with a Reichart Thermo apparatus and stereomicroscope, and are uncorrected.

The 100 MHz proton nuclear magnetic resonance (1H nmr) spectra were recorded with a JEOL-JNM-4H-100 spectrometer, and 300 MHz 1H nmr spectra with a Bruker AM 300 spectrometer. Tetramethylsilane (T.M.S.) or the sodium salt of 3-(trimethylsilyl)-1-(propanesulfonic acid) (D.S.S.) was used as an internal standard. Chemical shifts (δ) are given in parts per million (ppm) relative to the standard. Resonances are described as singlets (s), doublets (d), triplets (t), quartets (q), multiplets (m), or combinations thereof. Proton resonance assignments appear in one of two forms, eg, H(6) or H_B^6 . The former appears when no ambiguity in assignment is present, the latter when resonance is associated with a specific ring or group (with reference to text where required). All spectra were recorded in $CDCl_3$ except where stated otherwise.

The carbon-13 nuclear magnetic resonance (^{13}C nmr) spectra were determined with a Bruker AM 300 spectrometer, and chemical shifts (δ) are in ppm from internal T.M.S.

The COSY and ^{13}C - 1H correlation spectra were obtained using a Bruker AM 300 spectrometer and all chemical shifts (δ) are in ppm from internal T.M.S. In general, resolution in the two dimensional spectra is somewhat lower than in standard spectra due to storage limits for computation.

Infrared (I.R.) spectra were recorded on an Hitachi 270-30 Infrared spectrophotometer in wavenumbers (cm^{-1}) as Nujol and hexachlorobutadiene mulls (unless otherwise stated) between KBr plates. Far I.R. spectra were recorded with a Perkin Elmer 577 spectrophotometer ($600-200^{-1}$) as Nujol mulls between polyethylene

plates. Absorption bands are described as either strong (s), medium (m), or weak (w) in intensity.

Low and high resolution mass spectra (M.S.) were obtained from a Vacuum General Micromass 7070F Spectrometer using the direct insertion technique with an electron beam energy of 70 eV and a source temperature of 200°C. Peaks of more than 10% base peak intensity (I) (except for some parent ions) are reported in descending m/e ratio. High resolution and chemical ionisation mass measurements were obtained on this instrument using electron impact and ammonia ionisation, respectively.

Medium pressure column chromatography was carried out using Merck silica gel GF₂₅₄.

Molecular weights were determined with a Knauer vapour pressure osmometer in chloroform at 37°C for ca. $3 \times 10^{-2} M$ solutions.

General Reagents and Solvents

All general purpose solvents (A.R. grade) were used as received. For recrystallisation and column chromatography all solvents were distilled but dry solvents were not used unless stated otherwise. For preparations involving palladium(0) complexes distilled solvents were also degassed by passage of N₂ through the solvent while under reflux.

More specialised solvent and reagent purification is listed below, with the purification methods used similar to those recommended by Perrin, Armarego, and Perrin¹, and Vogel².

Acetic acid (glacial), refluxed and fractionally distilled from acetic anhydride and potassium permanganate.

Benzene, washed with conc. H₂SO₄, water, 2M NaOH, then refluxed and distilled from P₂O₅ and stored over sodium.

2-Benzylpyridine, vacuum distilled and stored over 4Å molecular sieves.

Bromobenzene, predried over CaCl₂, refluxed and distilled from Ca turnings, and stored over 4Å sieves.

2-Bromopyridine, predried over NaOH, distilled from CaO and stored over 4Å sieves.

Diethyl ether (ether), dried over 4Å sieves followed by reflux and distillation from sodium/benzophenone and stored over sodium.

Hexane, refluxed and distilled from sodium and stored over sodium.

Iodomethane, distilled and stored over 4Å sieves.

Tetrahydrofuran (THF) predried over KOH followed by reflux and distillation from sodium/benzophenone and stored over sodium.

Toluene, refluxed and distilled from sodium and stored over sodium.

All distillations were carried out under a nitrogen atmosphere.

All solid reagents were used as received after drying over P_2O_5 *in vacuo*.

Methylmercuric nitrate for synthetic studies was prepared by metathesis of silver nitrate and a slight excess of methylmercuric iodide (Alfa-Ventron) in water.

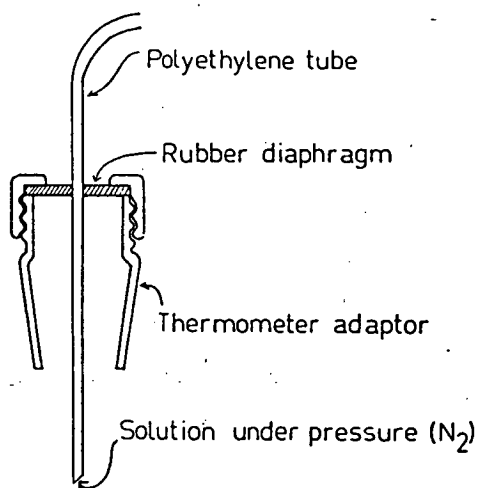
General Procedures using Solutions of Lithium Reagents

Some preparative procedures described in the following pages require the transfer of lithiated organic substrates in ethereal solvents. This may be performed by the use of septa and stainless steel cannulas, for large volumes of solution, or by syringe techniques for small volumes. However, the bore-size of cannulas and syringe needles available from commercial sources is often limited, and large bore devices frequently cause irreparable damage to septa.

In this study it has been found that polyethylene tubing is possibly more useful in transferring solutions, and solutions containing suspended solids. The tubing is commonly available from medical suppliers, is available in a large range of internal diameters, is readily cleaned and dried (hydrophobic surface), is flexible, and inexpensive. Adaptation of standard Quickfit thermometer adaptors by insertion of a rubber diaphragm (with hole) allows rapid flushing by inert gas and visible transfer of solutions. Solutions are transferred under inert gas pressure and siphoning is possible after addition has commenced. Solids in suspension may be satisfactorily transferred for addition or

filtration in a similar manner, under pressure, and blockages may be removed by flexing the tubing.

This method has been found to be useful in the transfer of phenyl-, butyl-, and methyllithium as well as for lithiated ligands. Temperature sensitive reagents such as 2-lithiopyridine may be transferred using this method with the inclusion of a polyethylene cooling jacket on exposed tubing. Suspended solids such as $[(dba)_2Pd]$ may also be transferred, without exposure to oxygen, by this method.



Polyethylene tube and cooling-jacket



Cold N₂ (cooling coil, slush bath)

Palladium Recovery³

Solutions containing Pd

All residue solutions were combined and evaporated to the lowest possible volume on a steam bath. The semi-solid residue was then transferred to a small crucible and placed on a sandbath over a hot plate and the temperature was gradually increased over ca. 10h. to maximum heating. (Too rapid increase in temperature causes spitting and is to be avoided as some losses may occur.) After virtually all liquids had been expelled the residues containing Pd and other inorganic salts were placed in a furnace and heated to 600-800° for at least 5 hours. On completion of firing the crucible was cooled slowly and the Pd metal, coated with oxide, and inorganic salts was removed to a conical beaker. The solids were then washed several times with boiling water (or soxhlet extracted) and isolated on a filter paper.

To effect the reduction of the oxides the palladium residue was placed in a glass tube which was then flushed in turn with N₂ then H₂. While under a steady stream of H₂ the residues were heated gently with a small spirit burner. After sufficient heating, initiating reaction, water was expelled and heat was evolved with scintillation of the metal as the oxide was consumed. (During the reduction the colour of the residue changes from near-black to light grey.) The residue was then heated and cooled under N₂ to expel absorbed hydrogen*.

The metal was then transferred to a conical beaker and was cautiously dissolved in *aqua regia*. When the metal had completely dissolved (some inorganic solids remain) the solution volume was lowered with heating and *conc.* HCl was added with heating until no more evolution of brown fumes was evident. The resulting deep red solution was then filtered to remove insoluble material and treated with *conc.* NH₄OH to precipitate impure [Pd(NH₃)₄][PdCl₄] (pink).

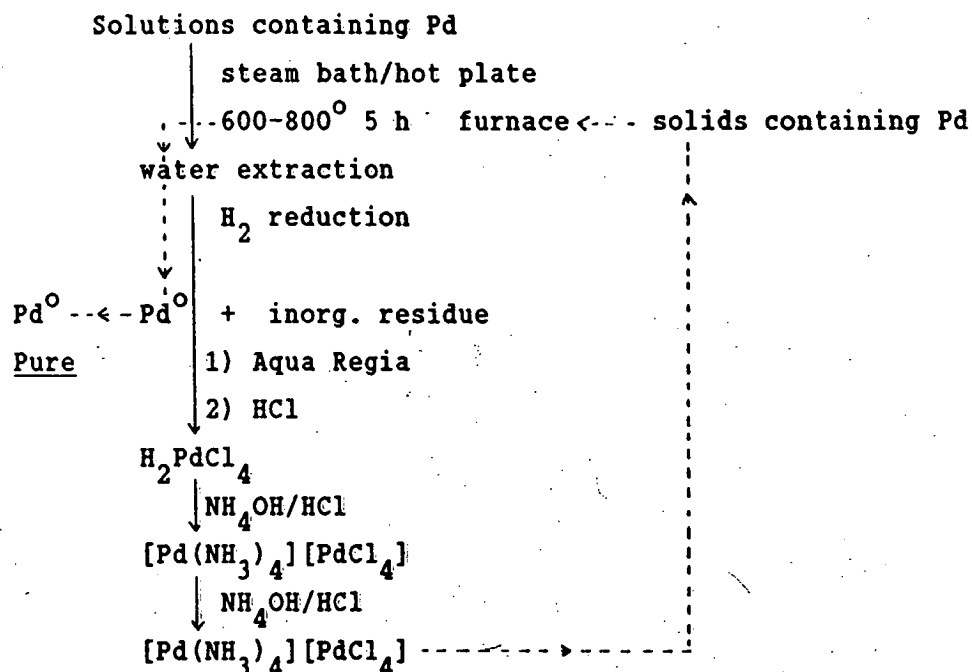
* Since finely divided palladium has a propensity to absorb large volumes of hydrogen it is inadvisable to expose even the cooled residue to oxygen as the metal will spontaneously inflame.

The impure product was again treated with NH_4OH and HCl to give pure $[\text{Pd}(\text{NH}_3)_4][\text{PdCl}_4]$. This solid was then returned through the firing and reduction sequences outlined to give very pure and highly reactive palladium sponge.

Solids containing Pd

Solids, such as filter papers, were carefully burnt and the ashes were included in the solution recovery. Solid samples were also included directly at that point.

Recovery Scheme



Palladium(II) and Palladium(0) Starting Materials

Palladous Chloride, PdCl_2

Palladium metal (from the Pd reduction process) was placed under a strong stream of Cl_2 gas. The solid was gently heated with a bunsen and after a short period of time the mass of finely divided metal was consumed with evolution of heat and production of the red-brown PdCl_2 in virtually quantitative yield.

Trans-Bis(benzonitrile)palladium(II) chloride, $[(\text{PhCN})_2\text{PdCl}_2]$.⁵

Palladous chloride was suspended in a large volume of benzonitrile and was heated with stirring to ca. 80°C. After the PdCl_2 had dissolved the solution was rapidly filtered (hot) and on cooling and addition of diethyl ether or petroleum-ether (40-60) the yellow complex, $[(\text{PhCN})_2\text{PdCl}_2]$, precipitated. The solid was isolated by filtration and washed with petrol. The filtrate containing benzonitrile was reserved for future similar preparations after removal of the precipitation solvent under vacuum.

Palladium Acetate, $\text{Pd}(\text{OAc})_2$.⁶

To a known quantity of palladium metal suspended in a large volume of glacial acetic acid was added a calculated slight deficiency of conc. HNO_3 and the solution was heated gently* until most of the palladium had dissolved. The mixture was then heated to reflux until no more brown fumes were evolved. (A period of 2-4h is usually necessary.) On completion of the reaction the deep red solution was rapidly filtered while hot and then allowed to cool slowly in a draught, depositing red-brown crystals of $\text{Pd}(\text{OAc})_2$.

The crude product was recrystallized by dissolving in a minimum quantity of warm benzene, dilution with an equivalent quantity of glacial acetic acid, and slow evaporation of the benzene, yielding pure $\text{Pd}(\text{OAc})_2$ as red crystals that go brownish on drying.

Trans-Bis(4-methylpyridine)palladium(II) chloride, $[(\gamma\text{-pic})_2\text{PdCl}_2]$.

To a benzene solution of $[(\text{PhCN})_2\text{PdCl}_2]$ was added a slight excess of 4-methylpyridine (γ -picoline) with stirring. Slow addition of petroleum ether (40-60) resulted in precipitation of the product as fine yellow needles in quantitative yield.

* This depends on the state of the metal. It is from Pd recovery and very finely divided prolonged heating is not required and the reaction with HNO_3 may be very vigorous, but if the Pd is commercial (fairly massive) heating may have to be applied for an extended period.

Sodium tetrachloropalladate, Na_2PdCl_4 .⁷

To an aqueous suspension of PdCl_2 was added a slight deficiency of NaCl (2 mole equivalents) with stirring. After one hour the deep red solution was filtered to remove excess PdCl_2 and the filtrate was taken to dryness under vacuum then dried under vacuum over P_2O_5 to give the product as a brown powder in quantitative yield (based on NaCl).

Bis(dibenzylideneacetone)palladium(0), $[(\text{dba})_2\text{Pd}]$.⁸

To a hot (60°C) methanolic solution containing dba (3 mol. equiv.) and sodium acetate (3 mol. equiv.) under N_2 was added an aqueous solution of Na_2PdCl_4 (1 mol. equiv.) with stirring. After maintaining heating for 15 min. the deep purple product was isolated by filtration under N_2 pressure and washed in turn with hot ethanol, water, and ethanol. Removal of solvent under vacuum with warming (60°C) gave the product as a deep red-purple microcrystalline powder in ca. 60% yield (some mechanical losses are incurred in transfers).

Complexes of Palladium(II) Acetate.

Trans-bis[α -phenyl- α -(pyridin-2-yl)toluene]palladium(II) acetate, $[(\text{pyPh}_2\text{CH})_2\text{Pd}(\text{OAc})_2]$

A solution of pyPh_2CH (0.860g, 0.35 mmol) in benzene (20 cm^3) was added to a filtered solution of palladium(II) acetate (0.399g, 0.18 mmol) in benzene (50 cm^3). On standing for 24h pale-yellow crystals of the complex formed and were collected (0.823g, 0.12 mmol, 66%, M.Pt. $145-147^\circ\text{C}$).

Analysis; Found (%), C 67.36, H 5.29, N 3.72

Calc. (%), C 67.18, H 5.07, N 3.92.

Infrared; 1594 (s,br), 1496 (m), 1482 (m), 1456 (m), 1436 (m),

1374 (s), 1360 (s), 1314 (s), 1158 (m), 758 (s),

738 (s), 700 (s), 666 (m), 606 (m), 496 (m).

¹H nmr (100 MHz);

9.48, m(br), H(6), 2H; 7.78, s, CH, 2H; 7.65-7.00, m,

H(3-5) and Ph, 26H; 1.30, s, CH_3 , 6H.

[Bis(pyridin-2-yl)methane]palladium(II) acetate, 0.5CHCl₃,
[(py₂CH₂)Pd(OAc)₂].0.5CHCl₃.

Under anhydrous conditions a filtered benzene solution (30 cm³) of py₂CH₂ (0.152g, 0.89 mmol) was added to a filtered benzene solution (50 cm³) of palladium(II) acetate (0.197g, 0.88 mmol). On standing the solution became orange/red, and after 2 days an orange solid had collected on the flask walls with some discharge of solution colour. The solvent was removed by decantation, the product dissolved in chloroform (10 cm³), filtered to remove some reddish gum, and dry petroleum ether added until cloudiness developed. On standing for 3h fine yellow crystals of the complex formed (0.282g, 0.55 mmol, 62%, M.Pt. 175°C, gradual dec.).

Analysis; Found (%), C 40.37, H 3.58, N 6.02

Calc. (%), C.40.91, H 3.66, N 6.17.

Solvate; CHCl₃, detection; M.S. (H.R.) found m/e 117.9120, calc. for ¹²C¹H³⁵Cl₃ 117.9144.

Infrared; 1608 (m), 1566 (s,br), 1480 (m), 1442 (m), 1394 (s), 1320 (m), 1230 (m), 1166 (m), 976 (m), 848 (m), 772 (m).

¹H nmr (100 MHz); 8.63, d, H(6), 2H, J(H(6,5) 4Hz);

7.95-7.65, m, 2H, and 7.55-7.15, m, 4H, H(3-5);

5.07, s, CH₂, 2H; 1.99, s, CH₃CO₂, 6H.

[α,α-Bis(pyridin-2-yl)toluene]palladium(II) acetate. 0.8C₆H₆
[(py₂PhCH)Pd(OAc)₂].0.8C₆H₆

On standing for a few minutes a benzene solution, obtained in a similar manner to that above, became deep red, and over a period of 12h the colour discharged to pale yellow with formation of fine yellow crystals. The crystals were collected under nitrogen, washed with benzene (2 x 20 cm³), and dried under a stream of nitrogen (0.0220g, 0.41 mmol, 60%, M.Pt. 175-177°C).

Analysis; Found (%), C 56.95, H 5.03, N 5.16

Calc. (%), C 57.03, H 4.89, N 5.36.

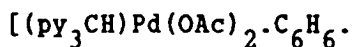
Solvate; C₆H₆, detection: microanalysis and ¹H nmr

Infrared; 1630 (s), 1600 (s), 1480 (s), 1376 (s), 1360 (s), 1306 (s), 1170 (m), 1160 (m), 974 (m), 682 (m).

¹H nmr (100 MHz);

8.24, d, H(6), 2H, J(H(6,5) 7Hz); 8.0-7.1, m, H(3-5) and Ph, 13H; 6.24, s, CH, 1H; 1.82, s, CH₃, 6H.

[Tris(pyridin-2-yl)methane]palladium(II) acetate. benzene



On standing for 10 min a yellow benzene solution, obtained in a similar manner to that above, became deep red, and over a period of 3 days the colour discharged to pale orange with formation of orange crystals. The crystals were collected and treated as above (0.081g, 46%, M.Pt. 137-140° dec.).

Analysis; Found (%), C 56.27, H 4.71, N 7.56.

Calc. (%), C 56.79, H 4.58, N 7.64

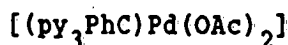
Solvate; C₆H₆, detection; M.S. (H.R.) found m/e 78.0456, calc. for 12 C₆H₆ 78.0479.

Infrared; 1594 (s,br), 1480 (m), 1436 (m), 1386 (s,br), 1334 (s,br), 1146 (m), 976 (m), 784 (m), 766 (m).

¹H nmr (100 MHz, -60°C);

9.04, d, H(6), 2H, J(H(6,5) 6Hz); 8.74, m(br), H(6), 1H; 8.10-7.00, m, H(3-5) and C₆H₆, 12H; 5.96, s, CH, 1H; 2.00, s, CH₃CO₂, 6H.

[α,α,α-Tris(pyridin-2-yl)toluene]palladium(II) acetate,



On standing for a few minutes a yellow toluene solution, obtained in a similar manner to the benzene solutions above, became slightly opaque and after 24h a fine yellow precipitate was evident. Large yellow plates formed over 4 days, and these were collected, washed with toluene (2 x 20 cm³), and dried in a stream of nitrogen (0.110g, 0.20 mmol, 63%, M.Pt. 198-200° dec.).

Analysis; Found (%), C 57.28, H 4.01, N 7.45.

Calc. (%), C 57.00, H 4.23, N 7.67.

Infrared; 1634 (s,br), 1582 (m), 1464 (m), 1440 (m), 1362 (s,br), 1308 (s), 1242 (m), 1168 (m), 992 (m), 766 (s), 718 (s,br), 678 (m).

¹H nmr (100 MHz);

9.05, d, H(6), 2H, J(H(6,5) 5Hz); 8.65, d, H(6), 1H, J(H(6,5) 6Hz); 7.8-6.6, m, H(3-5) and Ph, 14H; 1.80, s, CH₃CO₂, 6H.

Rac-[1,2-diphenyl-1,2-bis(pyridin-2-yl)ethane]palladium(II) acetate, $[(\text{pyPhCH})_2\text{Pd}(\text{OAc})_2]$.

A filtered solution of palladium(II) acetate (0.139g, 0.62 mmol) in benzene (30 cm³) was added to a filtered solution of 1,2-diphenyl-1,2-bis(pyridin-2-yl)ethane (0.362g, 1.08 mmol) in benzene (50 cm³) under nitrogen. On standing for 2 days in a sealed flask pale yellow needles formed with some discharge of the yellow colour from solution. Filtration and drying under a stream of nitrogen gave the complex as lemon yellow needles (0.114g, 0.20 mmol, M.Pt. 190-192°).

Analysis; Found (%), C 60.0, H 4.8, N 4.7

Calc. (%), C 60.0, H 4.7, N 5.0.

Infrared; 1640 (s), 1606 (s), 1494 (w), 1480 (m), 1454 (w), 1436 (m), 1382 (s), 1360 (s), 1314 (s), 1162 (w), 766 (m), 754 (m), 742 (w), 710 (m), 692 (m).

¹H nmr (300 MHz);

9.68, dd, H(6), 1H, J(H(6,5) 5.81Hz, H(6,4) 1.26Hz);
9.03, d, CH, 1H, J(CHCH 12.6Hz); 8.86, dd, H(6), 1H,
J(H(6,5) 5.34Hz, H(6,4) 0.94Hz); 8.04, d, 2H; 7.86, m,
2H; 7.54, m, 2H; 7.37, m, 2H; 7.29-7.21, m, C. 5H;
7.15-7.08, m, C. 3H; 4.99, d, CH, 1H, J(CHCH 12.6Hz),
2.06, s, CH₃CO₂, 3H; 1.97, s, CH₃CO₂, 3H.

see page 102 for ring assignments.

Bis[1,1,2,2-tetrakis(pyridin-2-yl)ethane]di(palladium(II) acetate), $[(\text{py}_2\text{CH})_2\text{Pd}(\text{OAc})_2]_2$.

Following a similar procedure to the above with palladium(II) acetate: ligand mole ratio 2:1, a yellow microcrystalline precipitate formed almost immediately upon mixing of benzene solutions. After collection and drying with nitrogen, a vacuum was required to remove residual benzene (64%, M.Pt. > 225°, dec.).

Analysis; Found (%), C 45.5, H 3.7, N 7.1

Calc. (%), C 45.8, H 3.8, N 7.1.

Infrared; 1634 (s), 1602 (s), 1480 (m), 1440 (m), 1374 (s), 1312 (s), 776 (m), 656 (m), 580 (m).

¹H nmr (300 MHz);

8.67, m, comprised of CH, s, 2H and H(6), dd, 4H, J(H(6,5) 5.9Hz, H(6,4) 0.3Hz); 8.40, dd, H(3), 4H, J(H(3,4) 7.83Hz, H(3,5) 0.81Hz); 7.65, m, H(4) or H(5), 4H; 7.22, m, H(5) or H(4), 4H; 2.10, s, CH₃CO₂, 12H.

See page 101 for assignments

[2,6-Bis[1,1-(pyridin-2-yl)ethyl]pyridine]
(acetato-0)palladium(II) acetate.trihydrate,
[{(py₂MeC)₂C₅H₃N}Pd(OAc)](OAc).3H₂O

A dichloromethane solution (10 cm³) of the ligand (0.476g, 1.07 mmol) and palladium(II) acetate (0.243g, 1.08 mmol) gave an orange oil on evaporation in a draught. The oil was dissolved in acetone (5 cm³), filtered, and diethyl ether added until cloudiness developed. On standing, the product formed as yellow microcrystals (0.460g, 59%, M.Pt. 172-3°).

Analysis; Found (%), C 54.6, H 5.0, N 9.3

Calc. (%), C 54.9, H 5.2, N 9.7.

Solvate; H₂O, detection; I.R., ¹H nmr (D₂O exchange).

Infrared; 3330 (s,v.br), 1600 (m,v.br.), 1464 (m), 1430 (w), 1370 (m,br), 1230 (m), 1170 (m), 974 (m), 774 (m), 730 (m).

¹H nmr (300 MHz);

8.43, t, H_B⁴, 1H, J(H^{4,3} = H^{5,4} 8.1Hz); 8.26, d, H_C⁶, 2H, J(H^{6,5} 4.3Hz); 8.18, m, H_A⁴, 2H; 8.08, m, H_B^{3,5} and H_A³, 4H; 7.91, dd, H_A⁶, 2H, J(H^{6,5} 5.6Hz, H^{6,4} 1.4Hz); 7.70, m, H_C⁴, 2H; 7.41, m, H_{A,C}⁵, 4H; 6.63, d, H_C³, 2H, J(H^{4,3} 7.9Hz); 5.03, s, H₂O, 6H, (variable); 2.40, s, CH₃, 6H; 2.01, s, CH₃CO₂, 6H.

See page 38 for ring assignments.

[Meso/Rac-2,6-bis{1-phenyl-1-(pyridin-2-yl)ethyl}pyridine]

(acetato-0)palladium(II) acetate. xH_2O ($x=1,3$),

Meso/Rac-[{(pyPhMeC)₂C₅H₃N}Pd(OAc)](OAc). xH_2O

Pale yellow crystals of the *meso* complex were obtained following a similar procedure to that above using the unseparated ligand and ether diffusion ($x = 3$) in a sealed chamber. Drying over P_2O_5 under vacuum gave the monohydrate ($x = 1$) in 37% yield (M.Pt. 153-155°). Using the pure *meso* ligand a yield of 85% was obtained.

Using the pure *racemic* ligand in a similar manner to the above gave the *racemic* complex as pale yellow crystals (66%, $x = 3$). The *racemic* complex is more soluble in acetone than the *meso* complex and tends to form an oil.

Analysis; *Meso*, Found (%), C 61.1, H 5.6, N 5.4.

($x=1$) Calc. (%), C 61.4, H 5.2, N 6.1.

Rac, Found (%), C 57.2, H 5.1, N 6.1.

($x=3$) Calc. (%), C 57.7, H 5.4, N 5.8.

1H nmr (300 MHz); *Meso* ($x=1$)

8.70, dd, H_A^6 , 1H, $J(H^{5,6})$ 5.27Hz, $H^{4,6}$ 1.17Hz; 8.48, m, H_C^5 , 1H; 8.34-8.22, m, $H_A^{3,4}$ and H_B^4 , 3H; 7.82-7.41, m (3 overlapping), H_C^4 (downfield, 1H), H_C^6 + 5Ph (6H), and H_A^5 + 2Ph (upfield, 3H); 7.18, m, H_C^5 + 3Ph, 4H; 6.88, m, H_B^3 , 1H; 6.80, m, H_C^3 , 1H; 3.30, s, Me_A , 3H; 2.53, s, Me_E , 3H; 1.93, s, CH_3CO_2 , 3H; 1.87, s, CH_3CO_2 , 3H.

N.B. i) For the *meso* complex with $x=3$ some broadened aromatic resonances are observed.

ii) Ring assignments are given on page 42, and the slight discrepancies in shift are a result of poorer resolution in the COSY spectrum. Those on page 42 have been taken from the COSY.

iii) The 1H nmr spectrum of the *racemic* complex is nearly identical to that given above although the *racemic* complex is composed of two conformers in solution.

Complexes of Palladium(II) Chloride

[Tris(pyrazol-1-yl)methane]palladium(II) chloride,
 $[(pz_3CH)PdCl_2]$.

Tris(pyrazol-1-yl)methane (0.542 g, 2.53 mmol) in benzene (30 cm³) was added to a solution of the benzonitrile complex $[(PhCN)_2PdCl_2]$ (0.945 g, 2.47 mmol) in benzene (50 cm³), and the mixture was stirred for 2h. Orange crystals of $[(pz_3CH)PdCl_2]$ were collected and washed with benzene (0.763 g, 79%, M.Pt. > 250°).

Analysis; Found (%), C 31.0, H 2.6, N 20.9, Cl 17.6.

Calc. (%), C 30.7, H 2.6, N 21.5, Cl 18.1.

Infrared; 1402 (s), 1300 (m), 1282 (m), 1218 (m), 1072 (m), 1042 (m), 842 (m), 812 (m), 796 (m), 770 (m), 756 (s), 746 (s).

¹H nmr (100 MHz); Insufficient solubility.

Trans-[bis(α-phenyl-α-(pyridin-2-yl)toluene)]palladium(II)
chloride.0.5C₆H₆, $[(pyPh_2CH)_2PdCl_2].0.5C_6H_6$.

In a manner similar to the above, the title complex was obtained as pale yellow crystals (78%, M.Pt. 236-238°).

Analysis; Found (%), C 66.65, H 4.72, N 3.69, Cl 9.9.

Calc. (%), C 66.26, H 4.71, N 3.96, Cl 10.0.

Solvate; C₆H₆, detection: ¹H nmr

Infrared; 1637(m), 1618(m), 1476(m), 1450(m), 1082(w), 1030(w), 764(s), 702(s), 679(w), 621(m), 497(s), 367(w), 337(s).

¹H nmr (100 MHz);

8.48, d, H(6), 2H, J(H(6,5) 5Hz); 7.55, s, CH, 2H;
 7.50-6.80, m, H(3-5) + Ph including solvate, 29H.

[α,α-Bis(pyridin-2-yl)toluene]palladium(II) chloride,
 $[(py_2PhCH)PdCl_2]$.

In a manner similar to the above the product was obtained as an orange powder (67%, M.Pt. > 250°).

Analysis; Found (%), C 48.48, H 3.50, N 6.61, Cl 16.7.

Calc. (%), C 48.20, H 3.33, N 6.61, Cl 16.7.

Infrared; 1598(m), 1570(m), 1489(m), 1253(m,br), 1078(m), 1069(m), 760(s), 755(s), 727(m), 701(s), 676(s,br), 620(m), 604(m).

^1H nmr (100 MHz); Insufficient solubility.

{ α,α,α -Tris(pyridin-2-yl)toluene}palladium(II) chloride.0.25CH₂Cl₂, [(py₃PhC)PdCl₂].0.25CH₂Cl₂.

In a manner similar to the above the product was obtained as an orange powder. Recrystallisation from CH₂Cl₂/petroleum ether (40-60) gave the product as a microcrystalline powder containing dichloromethane of crystallisation (49%, M.Pt. > 250°).

Analysis; Found (%), C 50.80, H 3.20, N 8.05, Cl 15.9.

Calc. (%), C 51.20, H 3.38, N 8.05, Cl 16.9.

Solvate; CH₂Cl₂, detection, M.S. (H.R.) Found 83.9530, calc. for C₁₂H₂Cl₂³⁵ 83.9537.

Infrared; 1593(m), 1572(m), 1489(m), 1473(m), 1462(s), 1431(s), 1305(w), 1271(w), 1246(w), 1192(w), 785(w), 758(s), 732(w), 707(m), 661(m).

^1H nmr (100 MHz); Insufficient solubility.

[Tris(pyridin-2-yl)methane]palladium(II) chloride, [(py₃CH)PdCl₂].

Tris(pyridin-2-yl)methane (1.03 g, 4.16 mmol) was dissolved in water (10 cm³) by the dropwise addition of HCl (5M), filtered, and added to a solution obtained similarly from palladium(II) chloride (0.736 g, 4.15 mmol) in water (10 cm³). Red-brown crystals formed immediately, and were collected and washed with water 30 min later (0.731 g, Found: C, 32.9; H, 2.6; N, 7.4; Cl, 24.6. Calc. for 'Pd₃[(py)₃CH]₂Cl₈.3H₂O': C, 33.3; H, 3.0; N, 7.3; Cl, 24.5%. Infrared absorption: 3460(w, v.br), 3108(m, v.br), 1618(w), 1604(w), 1478(w), 1458(w), 1442(w), 1404(s), 1298(w), 1190(w), 788(w), 773(w), 756(m), 720(m), 675(w), 658(w), 642(w), 612(w)). The clear orange filtrate was transferred to a sealed-chamber, and neutralized by slow transfer of NH₃(g) from a solution of conc. NH₄OH resulting in slow discharge of the orange colour and deposition of orange crystals. On clarification of the solution (2-3 h), the crystals of [(py₃CH)PdCl₂] were collected and washed with water (0.591 g, 33%, M.Pt. > 250°). Continued

neutralization of the resultant filtrate, in the same manner, gave crystals of py_3CH (0.31 g, 31%, ^1H nmr and I.R. identification).

Analysis; Found (%), C 45.0, H 3.2, N 9.9, Cl 17.2.

Calc. (%), C 45.3, H 3.1, N 9.9, Cl 16.7.

Infrared; 1612(w), 1582(w), 1462(w), 1404(m,br), 1310(w), 1152(w), 762(s), 630(m), 614(m).

^1H nmr (100 MHz); Insufficient solubility.

N.B. Attempted preparation using $[(\text{PhCN})_2\text{PdCl}_2]$ as described for $[(\text{pz}_3\text{CH})\text{PdCl}_2]$ resulted in precipitation of an orange insoluble powder of approximate composition $1\text{py}_3\text{CH} : 2\text{PdCl}_2$. Analysis; Found (%), C 32.43, H 2.13, N 6.61, Cl 26.2, calc. (%), for $[(\text{py}_3\text{CH})(\text{PdCl}_2)_2]$ C 31.93, H 2.18, N 6.98, Cl 23.56.

Meso-2,6-bis([1-phenyl-1-(pyridin-2-yl)ethyl]pyridine)(chloro) palladium(II) chloride dihydrate,

Meso- $[(\text{pyPhMeC})_2\text{C}_5\text{H}_3\text{N}]\text{PdCl}]\text{Cl} \cdot 2\text{H}_2\text{O}$.

To an acetone solution (5 cm^3) of the ligand (0.281 g, 0.64 mmol) was added an acetone solution (5 cm^3) of $[(\text{Me}_2\text{S})_2\text{PdCl}_2]^{20}$ (0.194 g, 0.64 mmol) and the combined solution was allowed to evaporate very slowly at room temperature to ca. 2 cm^3 . Pale yellow crystals of the crude product were then isolated by filtration and washed with a little acetone. The crude product was recrystallised by dissolution in 25 cm^3 of boiling water, filtering, and cooling and evaporation of the solution to ca. 10 cm^3 . The pure product (0.113 g, 0.17 mmol, 27%) was isolated by filtration and dried *in vacuo* at 80° for 2h (0.113 g, 0.17 mmol, 27%, M.Pt. 201-203°).

The complex may also be prepared by quantitative metathesis with NaCl from the analogous acetato-complex in a small volume of water.

Analysis; Found (%), C 56.27, H 4.35, N 7.09, Cl 10.4.

Calc. (%), C 56.85, H 4.77, N 6.42, Cl 10.8.

Solvate; H_2O , detection; ^1H nmr (D_2O exchange), I.R.

Infrared; 3440(s,v.br), 1600(s), 1588(s), 1574(s), 1496(m), 1472(s), 1456(s), 1446(s), 1370(m), 1300(m), 1166(m), 1060(m), 860(m), 798(s), 784(s), 706(s), 598(m), 578(m).

^1H nmr (100 MHz)

8.97, dd, H_A^6 , 1H, $J(\text{H}^{5,6})$, 5.7Hz, $\text{H}^{4,6}$ 1.4Hz; 8.72, m, H^B , 1H; 8.47-8.23, m, $\text{H}_\text{A}^{3,4} + \text{H}_\text{C}^4$, 3H; 7.99, dd, H_C^6 , 1H, $J(\text{H}^{5,6})$ 5.7Hz, $\text{H}^{6,4}$ 1.6Hz; 7.69-7.43, m, 9H; 7.19-7.13, m, 2H; 6.97-6.91, m, 2H; 6.83, m, H_B^3 , 1H; 6.58, m, H_C^3 , 1H; 3.20, s, Me_A , 3H; 2.63, s, Me_E , 3H; 1.76, s(br), H_2O (variable).

Palladium(II) Cationic and Neutral Complexes of the type
 $[\text{L}_2\text{Pd}](\text{X})_2$ and $[\text{L}_2\text{Pd}]$.

$[\text{Bis}\{\text{tris}(\text{pyrazol-1-yl})\text{borato}\}]\text{palladium(II)}$,
 $[(\text{pz}_3\text{BH})_2\text{Pd}]$.

Potassium tris(pyrazol-1-yl)borate (1.895g, 7.52 mmol) in water (20 cm^3) was added to a filtered solution obtained by addition of HCl (5M) to palladium(II) chloride (0.635g, 3.58 mmol) in water (10 cm^3) until the PdCl_2 had just dissolved, resulting in a discharge of colour from red-brown to pale-yellow and formation of a tan precipitate. The solution was made slightly alkaline (to litmus) by addition of NaOH solution, and the off-white precipitate was collected and washed with a large quantity of water. The crude product was dried, and recrystallised quickly from boiling ethanol to give pale-yellow crystals of $[(\text{pz}_3\text{BH})_2\text{Pd}]$ on cooling (1.271g, 67%. M.Pt. 155-160 dec.).

Analysis; Found (%), C 40.57, H 3.65, N 31.34.

Calc. (%), C 40.60, H 3.79, N 31.57.

Infrared; 3124 (m,br), 2440 (w), 1504 (m), 1402 (s), 1322 (m), 1284 (m), 1235 (m), 1222 (m), 1126 (m), 1114 (m), 1078 (m), 1062 (m), 1034 (m), 960 (m), 918 (m), 770 (m), 756 (m), 654 (w), 618 (w).

^1H nmr (100 MHz) 7.90-7.30, three broadened overlapping resonances (maxima: 7.80, 7.61, 7.42), 8H; 7.08, m, 4H; 6.27, m, 8H (broad).

[Bis-{tris(pyridin-2-yl)methane}]palladium(II) nitrate,
 $[(\text{py}_3\text{CH})_2\text{Pd}](\text{NO}_3)_2$.

Silver nitrate (0.471g, 2.77 mmol) was added to a suspension of $[(\text{py}_3\text{CH})\text{PdCl}_2]$ (0.591g, 1.39 mmol) in water (20 cm³) and stirred in darkness for 2h, followed by removal of silver chloride to give a bright yellow filtrate. Further tris(pyridin-2-yl)methane (0.335g, 1.36 mmol) was added to the filtrate with stirring, and rapidly dissolved to give a pale yellow solution. The solution was filtered, and allowed to evaporate in a draught to give the crude product as a pale yellow crystalline solid. Recrystallisation from water with slow evaporation gave $[(\text{py}_3\text{CH})_2\text{Pd}](\text{NO}_3)_2$ as pale yellow crystals (0.4g, 41%, M.Pt. > 250°).

Analysis; Found (%), C 52.98, H 3.54, N 15.10.

Calc. (%), C 53.01, H 3.61, N 15.46.

Infrared; 1608 (m), 1586 (m), 1568(m), 1474 (m), 1444 (m), 1428(m), 1340 (s, v.br), 1150 (m), 992 (m), 780 (s), 644 (m), 632 (m).

^1H nmr (100 MHz, D₂O, D.S.S. lock); 8.84, d, H(6), 2H, J(H(6,5) 4Hz) (uncoordinated); 8.40-8.00, m, 10H; 7.95, d, H(6), 4H, J(H(6,5) 5Hz) (coordinated); 7.80-7.30, m, 8H; 6.94, s, 2H, CH.

[Bis{tris(pyrazol-1-yl)methane}]palladium(II) nitrate and tetrafluoroborate,

$[(\text{pz}_3\text{CH})_2\text{Pd}](\text{X})_2$, where $\text{X} = \text{NO}_3^-$, BF_4^- .

These complexes were prepared in a similar manner to $[(\text{py}_3\text{CH})_2\text{Pd}](\text{NO}_3)_2$ using AgNO_3 and AgBF_4 salts, respectively, giving pale yellow crystals for $\text{X} = \text{NO}_3$ (62%, M.Pt. 183-185°), and yellow crystals for $\text{X} = \text{BF}_4$ (58%, M.Pt. 226-230°).

$\text{X} = \text{NO}_3$

Analysis; Found (%), C 36.17, H 2.75, N 30.20.

Calc. (%), C 36.46, H 3.06, N 29.76.

Infrared; 1516 (m), 1470 (m), ca 1362 (s, v.br), 1102 (m), 1090 (m), 1074 (m), 1048 (m), 960 (m), 844 (m), 804 (m), 788 (m), 766 (s), 598 (m).

^1H nmr (100 MHz, CD_3OD), 9.60, s, CH, 2H; 8.34, m(br.), 6H; 7.66, m, 6H; 6.60, m, 6H.

$\text{X} = \text{BF}_4$

Analysis; Found (%), C 34.04, H 3.28, N 23.72.

Calc. (%), C 33.91, H 2.85, N 23.72.

Infrared; 1516 (w), 1642 (w), 1414 (s, br), 1328 (m), 1300 (s), 1272 (m), 1078 and 1032 (minima of a strong broad absorption), 846 (m), 798 (m), 766 (s), 602 (m), 520 (m).

^1H nmr (100 MHz); Insufficient solubility.

[Bis{tris(pyrazol-1-yl)methane}]palladium(II) perchlorate,

$[(\text{pz}_3\text{CH})_2\text{Pd}](\text{ClO}_4)_2$

This complex was prepared in a similar manner to the complexes above except that an aqueous solution of two equivalents of AgClO_4 was generated by addition of standardised perchloric acid to an excess quantity of freshly collected silver(I) oxide followed by filtration. Pale yellow crystals of the complex were collected (75%, M.Pt. ca. 240° dec.).

Analysis; Found (%), C 32.56, H 2.93, N 22.39.

Calc. (%), C 32.74, H 2.75, N 22.91.

Infrared; 1518 (w), 1462 (w), 1410 (s,br), 1300 (m), 1096 and 1074 (as part of a strong broad absorption), 768(s), 624 (m).

^1H nmr (100 MHz); Insufficient solubility.

Cyclometallation Products from Palladium(II) Acetate.

Di[$\{\alpha\text{-(phenyl-C}^2\text{)-}\alpha\text{-(pyridin-2-yl-M)toluene}\}$
 $\{\mu\text{-acetato}\}$ palladium(II)] \cdot dichloromethane
 $\{[\text{pyPhHC}(\text{C}_6\text{H}_4)]\text{Pd}(\text{OAc})\}_2\cdot\text{CH}_2\text{Cl}_2$.

Solid pyPh_2CH (0.260g, 1.06 mmol) was added to a warmed solution of palladium(II) acetate (0.248 g, 0.11 mmol) in glacial acetic acid (40 cm^3), and the solution refluxed for 30 min. On cooling, the solvent was removed with warming in a vacuum to give an oil containing crystals and traces of acetic acid. The product was dissolved in dichloromethane (15 cm^3), filtered, and petroleum ether added until cloudiness developed. Pale yellow crystals formed on standing and these were collected and recrystallised from dichloromethane/petroleum ether (0.268 g, 0.57 mmol, 54%, M.Pt. $>250^\circ$).

Analysis; Found (%), C 54.6, H 4.2, N 3.4.

Calc. (%), C 54.5, H 3.9, N 2.9.

Solvate; CH_2Cl_2 ; detection, M.S. (H.R.) found m/e 83.9526, calc. for $^{12}\text{C}^1\text{H}_2^{35}\text{Cl}_2$ 83.9534.

Infrared; 1586(s), 1558(m), 1416(s), 1154(m), 1034(m), 974(m), 750(s), 728(s), 686(m), 626(m), 608(m).

^1H nmr (100 MHz) Insufficient solubility.

Di[$\{\alpha\text{-(phenyl-C}^2\text{)-}\alpha\text{-(pyridin-2-yl-M)toluene}\}$
 $\{\mu\text{-chloro}\}$ palladium(II)] \cdot
 $\{[\text{pyPhHC}(\text{C}_6\text{H}_4)]\text{PdCl}\}_2$.

Sodium chloride (0.094 g, 2.65 mmol) was added to a stirred suspension of the above (0.166 g, 0.19 mmol) in 2:1 acetone/water (30 cm^3). After stirring for 20h the pale cream product was collected and washed with water (0.132 g, 0.171 mmol, 90%, M.Pt. $>250^\circ$).

Analysis; Found (%), C 55.7, H 3.6, N 3.3, Cl 9.2.

Calc. (%), C 56.0, H 3.6, N 3.6, Cl 9.2.

Infrared; 1608(m), 1574(w), 1564(w), 1494(w), 1442(m), 1402(w), 156(m), 1032(m), 972(w), 752(s), 728(m), 696(m), 608(m).

¹H nmr (100 MHz); Insufficient solubility.

[[α -(phenyl- C^2)- α -(pyridin-2-yl-*M*)toluene]
(acetylacetonato-*O, O'*)palladium(II)]
[[pyPhHC(C₆H₄)Pd(acac)].

Acetylacetonatothallium(I) (0.092 g, 0.303 mmol) was added to a stirred suspension of the above (0.114 g, 0.148 mmol) in dichloromethane (20 cm³), to give immediate precipitation of thallos chloride. After stirring for 1h the precipitate was removed by filtration, and the filtrate was reduced in volume under vacuum to give a near colourless gum. The gum was dissolved in benzene (5 cm³) and petroleum ether was added until cloudiness developed. A colourless microcrystalline solid formed on standing (0.044 g, 0.098 mmol, 66%, M.Pt. 206-207°).

Analysis; Found (%), C 61.3, H 5.0, N 3.1

Calc. (%), C 61.4, H 4.7, N 3.1

Infrared; 1596(s), 1516(s), 1448(w), 1394(s), 1262(m), 1156(m), 1020(m,br), 932(m), 772(s), 744(s), 694(s), 628(m), 608(s).

¹H nmr (100 MHz);

8.81, d, H(6), 1H, J(H(6,5) 5.0Hz); 7.7-7.3, m, and 7.26, 6.90, m, H(3-5) and Ph, 12H; 5.46, s, CH, 1H; 5.23, s, CH of acac, 1H; 1.99, s, and 1.91, s, CH₃, 6H.

Mass Spectrum (m/e, I%)

450 (M⁺) and 350 (isotopic clusters of 7 lines each) 1.5% and 2.5% resp., 245(30), 244(9), 243(55), 167(18), 165(18), 100(40).

[[1,3-Bis[1-(pyridin-2-yl-*M*)ethyl](phenyl- C^2)]
(acetato-*O*)palladium(II)]
[[pyMeHC)₂C₆H₃]Pd(OAc)].

A solution of palladium(II) acetate (0.595 g, 2.65 mmol) and ligand (0.642 g, 2.23 mmol) in glacial acetic acid (40 cm³) was heated on a steam bath for 12h, filtered while hot, and most of the solvent was removed in a vacuum to give a brown oil. The oil was dissolved in chloroform (40 cm³) and treated with a saturated

solution of aqueous sodium carbonate. The organic phase was isolated, dried over magnesium sulfate, filtered, and reduced to dryness to give a pale brown foam. Chromatographic separation of the foam (medium pressure silica column, $\text{CHCl}_3/\text{MeOH}$ -5%) gave the product (R_f 0.24, in the same solvent) as a near colourless foam on removal of solvent. Addition of acetone (5 cm^3) gave an initial crop of colourless crystals with a further crop obtained on exposure to ether vapour in a sealed chamber (0.711 g, 1.57 mmol, 71%, M.Pt. ca. 240° dec.).

Analysis; Found (%), C 58.37, H 5.21, N 5.73.

Calc. (%), C 58.35, H 4.90, N 6.19.

Infrared; 1596(s,br), 1568(m,br), 1482(m), 1428(m), 1384(s,br), 1328(m), 1156(m), 814(m), 776(m), 758(s), 730(s), 666(s).

^1H nmr (300 MHz);

9.08-8.96, m, H_A^6 and H_C^6 , 2H; 7.77-7.68, m, H_A^4 and H_C^4 ; 7.43, m, H_A^3 and H_C^3 , 2H; 7.23-7.15, m, H_A^5 and H_C^5 , 2H; 7.03-6.91, m, Ph, 3H; 5.01, q, CH, ca. 0.5H, $J(\text{CHCH}_3$ 6.8Hz); 4.34, q, CH, ca. 1.5H, $J(\text{CHCH}_3$ ca. 7.2Hz); 2.33, d, CH_3 , ca. 4H, $J(\text{CH}_3\text{CH}$ 7.2Hz); 2.04, s, CH_3CO_2 , 3H; 1.83, d, CH_3 , ca. 2H, $J(\text{CH}_3\text{CH}$ 6.8Hz).

N.B. The spectrum represents a mixture of *meso* and *racemic* complexes. Details of spectral interpretation are given on page 71 with ring assignments.

Osmometric Molecular Weight; Found 429, calc. 453.

[[1,3-Bis[1-(pyridin-2-yl-Methyl)](C₆H₅)₂]
(chloro)palladium(II)]
[(pyMeHC)₂C₆H₃]PdCl].

Sodium chloride (0.119 g, 2.04 mmol) was added to a stirred suspension of the above (0.614 g, 1.36 mmol) in acetone/water (2:1, 20 cm^3) rapidly producing a white flocculent suspension. After stirring for 2h the product was filtered off, washed with water ($3 \times 50\text{ cm}^3$), and dried under vacuum over P_2O_5 (0.534 g, 1.24 mmol, 91%, M.Pt. $>250^\circ$).

Analysis; Found (%), C 55.8, H 4.4, N 6.5, Cl 8.2.

Calc. (%), C 56.0, H 4.5, N 6.5, Cl 8.3.

Infrared; 1602(m), 1564(w), 1480(m), 1430(m,br), 1280(w), 1246(w), 1158(m), 814(m), 784(m), 776(m), 760(s), 598(w), 564(w), 542(w), 510(w).

¹H nmr (300 MHz);

9.47, d, H_R⁶, J(H^{6,5} 4.4Hz) and 9.39, m, H_M⁶, 2H; 7.70, m, H⁴, 2H; 7.43, m, H³, 2H; 7.18, m, H⁵, 2H; 6.98, m, Ph, 3H; 5.03, q(br), CH *Meso*, and 4.35, q(br), CH *Rac.*, 2H; 2.31, m, CH₃ *Meso* and *Rac.*, and 1.84, d, CH₃ *Meso*, 6H.

- N.B.
- i) H(3-5) and Ph are the sum of coincident resonances of the *Meso* (M) and *Rac.* (R) complexes.
 - ii) The ratio of *Meso*:*Rac.* is approximately 4:3 and the spectral assignments are discussed in detail on pages 63-69.

[[1,3-Bis[1-(pyridin-2-yl)-*N*ethyl] (phenyl-C²)] (aquo)palladium(II)]tetrafluoroborate.hemihydrate.
[(pyMeHC)₂C₆H₃]Pd(H₂O)]BF₄·0.5H₂O.

A suspension of the above (0.472 g, 1.10 mmol) in acetone (15 cm³) was treated with an aqueous solution (5 cm³) of AgBF₄ (0.211 g, 1.08 mmol) and was stirred for 6h. After removal of precipitated AgCl the filtrate was slowly evaporated in a draught depositing colourless flocculent crystals of the product. The product was recrystallised from acetone (0.393 g, 0.77 mmol, 72%, M.Pt. 167-168°).

Analysis; Found (%), C 47.2, H 4.4, N 5.5.

Calc. (%), C 47.3, H 4.4, N 5.5.

Infrared; 3500 (v.s, v.br), 1642(m,br), 1608(s), 1574(w), 1484(m), 1458(m), 1064(v.s, v.br), 812(m), 788(m), 778(m), 760(s), 732(s).

¹H nmr (300 MHz); Insufficient Solubility.

$[(1,3\text{-Bis}[(\text{pyridin-2-yl-}M)\text{methanonyl}](\text{benzene-}C^2)]$
 $(\text{acetato-}O)\text{palladium(II)}]$,
 $[(\text{pyOC})_2C_6H_3]\text{Pd(OAc)}]$.

In a similar manner to the preparation of $[(\text{pyMeHC})_2C_6H_3]\text{Pd(OAc)}$ the complex was obtained in 72% yield from $\text{CH}_2\text{Cl}_2/\text{acetone}$ as a pale yellow crystalline solid (M.Pt. $>250^\circ$).

Analysis; Found (%), C 52.87, H 3.12, N 6.18.

Calc. (%), C 53.06, H 3.12, N 6.19.

Infrared; 1660(s), 1616(s), 1590(s), 1442(m), 1374(m), 1280(m), 1242(m), 1156(m), 832(m), 754(s), 716(s), 666(s).

^1H nmr (300 MHz);

9.14, dd, H(6), 2H, $J(\text{H}(6,5)) = 5.7\text{Hz}$, $J(\text{H}(6,4)) = 1.4\text{Hz}$;
 8.28, d, Ph H(6) and H(4), 2H, $J(\text{H}(6,5)) = J(\text{H}(4,5)) = 7.8\text{Hz}$;
 8.08, td, H(4), 2H, $J(\text{H}(4,3)) = J(\text{H}(4,5)) = 7.7\text{Hz}$,
 $J(\text{H}(4,6)) = 1.4\text{Hz}$;
 7.92, dd, H(3), 2H, $J(\text{H}(3,4)) = 7.7\text{Hz}$,
 $J(\text{H}(3,5)) = 1.2\text{Hz}$;
 7.57, ddd, H(5), 2H, $J(\text{H}(5,4)) = 7.7\text{Hz}$,
 $J(\text{H}(5,6)) = 5.7\text{Hz}$, $J(\text{H}(5,3)) = 1.2\text{Hz}$;
 7.34, t, Ph H(5), 1H,
 $J(\text{H}(5,4)) = J(\text{H}(5,6)) = 7.8\text{Hz}$;
 1.99, s, CH_3CO_2 , 3H.

Osmometric Molecular Weight;

Found, 465; calc. 452.

Methylmercury(II) Nitrate Complexes of $(\text{pyPhMeC})_2C_5H_3N$

A filtered solution of $(\text{pyPhMeC})_2C_5H_3N, L$, (1.433g, 3.2 mmol) in acetone (15 cm^3) was added to a filtered solution of methylmercury(II) nitrate (0.901g, 3.2 mmol) in acetone (30 cm^3). The solution was allowed to evaporate in a draught at ambient temperature to a volume of ca. 20 cm^3 over a 2-3h period, and colourless crystals of *Meso*- $[\text{LHgMe}]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ were collected and air dried (1.352g). The filtrate was transferred to a sealed chamber containing a beaker of diethyl ether, and on slow diffusion of ether vapour into the acetone solution two crops of *Rac*- $[\text{LHgMe}]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ were obtained and combined (0.420g, 13%). The *meso* complex was recrystallised by dissolution in warm acetone (60 cm^3) and evaporation to ca. 30 cm^3 to give colourless

crystals (0.494 g). Further crops were obtained on continued volume reduction to give an overall yield of 1.087g (44%).

Meso-[LHgMe]NO₃·2H₂O.

Analysis; Found (%), C 51.5, H 4.6, Hg 27.9.

Calc. (%), C 50.9, H 4.5, Hg 26.7.

Infrared; 3570(vw,vb), 3468(w,vb), 3128(vw), 3058(vw), 2988(w), 1590(m) and 1580(m), 1494(w), 1470(m), 1448(m), 1380(vs) and 1330(vs,b) and 1292(m) as part of broad $\nu(\text{NO}_3^-)$, 1190(w), 1157(w), 1137(vw), 1112(vw), 1070(w), 1050(w), 1025(w), 1013(w) and 1004(m), 912(vw,b), 890(w), 841(vw), 829(w), 789(w), 774(m) and 764(s), 693(s), 648(w), 639(w), 630(m), 618(m), 595(w), 572(m) and 566(w).

¹H nmr (300 MHz);

8.55, m, H(6) (pyridines), 2H, J(H(6.5) 5.3Hz); 8.12-8.07, m, 1H; 8.00-7.87, m, 6H; 7.51-7.46, m, 2H; 7.35-7.22, m, 6H; 6.84-6.80, m, 4H; -0.35, s with coupling to ¹⁹⁹Hg, 3H, ²J(¹H-¹⁹⁹Hg) 256.6Hz.

Rac-[LHgMe]NO₃·2H₂O

Analysis; Found (%), C 51.8, H 5.0, Hg 27.4.

Calc. (%), C 50.9, H 4.5, Hg 26.7.

Infrared; 3550(vw,vb), 3456(w,vb), 3060(w), 2916(w), 1588(m) and 1578(m), 1494(w), 1470(m), 1448(m), 1376(vs,b) and 1330(vs,b) and 1292(m) as part of broad $\nu(\text{NO}_3^-)$, 1160(w,b), 1137(vw), 1112(vw), 1068(w,b), 1049(vw,b), 1024(vw), 1011(vw), 1002(w), 976(w,b), 868(vw), 848(vw,b), 830(vw), 762(m), 698(m), 648(w), 640(vw), 630(w), 616(m), 594(m), 574(m) and 566(m).

¹H nmr (300 MHz); As for meso-L complex.

Isolation of meso-L and rac-L from the Hg(II)Me Complexes.-

An identical procedure was used for both diastereoisomers, and the isolation of meso-L is given as an example. The Hg(II)Me complex (0.088g, 0.12 mmol) was suspended in water (15 cm³) and

sodium cyanide (0.0067g, 0.14 mmol) was added with stirring. After stirring for 20h the ligand was isolated by filtration using a fine sinter, washed with a large volume of water, dried in air, and then under vacuum (0.0447g, 0.1 mmol, 86%).

Meso-L.

Infrared; 3064(vw,b), 2984(vw,b), 1586(w) and 1571(w), 1496(w), 1470(m), 1446(m), 1430(m), 1370(w,b), 1206(vw,b), 1160(w,b), 1080(vw) and 1068(vw), 1026(w), 990(vw) and 973(w,b), 866(vw), 786(vw), 744(w), 698(w), 644(vw), 630(vw), 614(vw), 577(w,b).

¹H nmr (300 MHz) 8.55, m, H(6) (pyridines), 2H, J(H(6,5) 4.8Hz); 7.62, m, 1H; 7.52, m, 2H; 7.25-7.14, m, including intense peaks at 7.22, 7.20, 7.16, 7.14; 7.06, m, 2H; 7.0-6.92, m.

Rac.-L

Infrared; 3060(vw,b), 2996(w,b), 1585(w) and 1569(w), 1496(w), 1470(m), 1446(m), 1430(m), 1372(w,b), 1210(vw,b), 1160(w,b), 1080(vw) and 1068(vw), 1026(w), 992(vw) and 974(w,b), 847(vw), 816(vw), 793(vw), 771(w), 744(w), 700(w), 646(vw) and 632(vw), 551(vw).

¹H nmr (300 MHz); 8.54, m, H(6) (pyridines), 2H, J(H(6,5) 4.8Hz); 7.54, m, 2H; 7.43, m, 2H; 7.24-7.16, m, including intense peaks at 7.21, 7.19, 7.18; 7.1-7.08, m, 2H; 7.05, m, 2H; 7.02-6.43, m.

Ligand Dimerisation using Mercury(II) Iodide

Bis(pyridin-2-yl)methane.

py₂CH₂.

An orange solution containing an orange precipitate was obtained on addition of butyllithium (0.4M, 12 cm³, 4.8 mmol, in hexane) to a solution of bis(pyridin-2-yl)methane (0.806 g, 4.7 mmol) in tetrahydrofuran (30 cm³) under nitrogen. After stirring for 15 min. a solution of mercury(II) iodide (1.077 g, 2.4 mmol) in tetrahydrofuran (30 cm³) was added rapidly dropwise. The colour of the solution partly discharged, and on reflux for 4h the orange colour completely discharged and metallic mercury was

deposited. On hydrolysis with water (2 cm³), all solvents were removed under vacuum, and the resulting residue was extracted with boiling ethanol and filtered. On cooling the filtrate, colourless crystals were deposited and collected and on reduction of filtrate volume further crops were obtained. Recrystallisation from hot ethanol, and vacuum drying at 80° for 4h gave colourless crystals of 1,1,2,2-tetrakis(pyridin-2-yl)ethane, (py₂CH)₂ (0.678 g, 85%, M.Pt. sublimes above ca. 230°).

Analysis; Found (%), C 76.8, H 5.1, N 16.3.

Calc. (%), C 77.4, H 5.8, N 16.8.

Infrared; 1588(m), 1568(m), 1470(m,br), 1432(m), 1216(w), 1150(w), 994(w), 766(s), 748(s), 728(m), 612(s), 558(m), 572(m).

¹H nmr (300 MHz);

8.44, m, H(6), 4H, J(H(6,5) 4.8Hz); 7.41, m, H(5,3), 8H; 6.90, m, H(4), 4H; 5.74, s, CH, 2H.

Mass Spectrum (m/e, I%);

339 (M+1⁺, 18%), 338(75), 337(20), 261(20), 260(88), 259(16), 258(20), 247(18), 246(100), 170(20), 169(95), 168(25).

Osmometric Molecular Weight, Found 327, calc. 338.

pyPhCH₂, pyPhMeCH, pyMe₂CH and py₂MeCH.-

Reaction as above gave colourless solutions with precipitation of mercury within 1-2 minutes at ambient temperature, to give, respectively, 1,2-diphenyl-1,2-bis(pyridin-2-yl)ethane, (pyPhCH)₂, recrystallised from hot ethanol or benzene (80%, M.Pt. 240-242°, lit. 244-248° (ref. 9a) 243-244° (ref. 9b), 240-241° (ref. 9c), 237-239° (ref. 9d)).

Infrared; 1588(m), 1568(w), 1494(m), 1472(m), 1434(s), 1144(m), 994(w), 744(s,br), 698(s), 612(s).

¹H nmr (300 MHz);

8.47, ddd, H(6), 0.8H, J(H(6,5) 4.83 Hz, H(6,4) 1.66 Hz, H(6,3) 0.76 Hz); 8.41, ddd, H(6), 1.2H, J(H(6,5) 4.82 Hz, H(6,4) 1.64 Hz, H(6,3) 0.76Hz); 7.47-6.87,

complex multiplets, H(3-5) and Ph, 6H; 5.28, s, CH, 0.6H; 5.26, s, CH, 0.4H.

Mass Spectrum (m/e, I%)

336 (M^+ , 22%), 335(19), 258(10), 245(20), 169(35), 168(100), 167(60).

Osmometric Molecular Weight; Found 350, calc. 336.

2,3-diphenyl-2,3-bis(pyridin-2-yl)butane, (pyPhMeC)₂, from ethanol, 42%, M.Pt. 131-134°.

Infrared; 1586(s), 1568(s), 1496(m), 1470(m), 1444(m), 1428(m), 1370(m), 1156(m), 1046(m), 1030(m), 810(s), 758(m), 742(s), 702(s), 656(s), 544(m).

Analysis; Found (%), C 85.7, H 6.7, N 7.7.

Calc. (%), C 85.7, H 6.7, N 7.7.

¹H nmr (300 MHz)

8.37, m, 1.5H, J(H(6,5) 4.5Hz); 8.16, m, H(6), 0.5H, J(H(6,5) 4.8Hz); 7.45, m, H(4) or H(5), 1.5H; 7.38, m, H(5) or H(4), 0.5H; 7.28-6.78, m, H(3) and H(4) or H(5), 4H; 2.20, s, Me, 6H.

Mass Spectrum (m/e, I%)

364 (M^+ , 22%), 363(26), 362(20), 361(23), 183(27), 182(60), 181(35), 180(100), 168(25), 167(40).

Osmometric Molecular Weight; Found 358, calc. 364.

2,3-dimethyl-2,3-bis(pyridin-2-yl)butane, (pyMe₂C)₂, from ethanol, 16% M.Pt. 116-117° (lit. 121°, ref. 10).

Infrared; 1486(s), 1568(m), 1470(s), 1428(s), 1380(m), 1154(s), 1098(m), 1050(m), 992(m), 796(s), 748(s), 596(s).

¹H nmr (100 MHz);

8.50, d, H(6), 2H, J(H(6,5) 5.0Hz); 7.35, m, H(4), 2H; 7.05-6.75, m, H(5,3), 4h; 1.40, s, Me, 12H.

Mass Spectrum (m/e, I%)

240 (M^+ , 15%), 121(100), 106(22), 92(17).

Osmometric Molecular Weight; Found 245, calc. 240.

2,2,3,3-tetrakis(pyridin-2-yl)butane, (py₂MeC)₂, from diethyl ether/hexane, 59%, M.Pt. 103-104°.

Analysis; Found (%), C 78.4, H 6.1, N 15.1.

Calc. (%), C 78.7, H 6.1, N 15.3.

Infrared; 1582(s), 1568(s), 1468(s), 1428(s), 1152(m), 1046(m), 990(m), 833(m), 810(m), 774(s), 748(s), 644(m), 616(m), 548(m).

¹H nmr (300 MHz);

8.35, d, H(6), 4H, J(H(6,5) 3.71Hz); 7.36, m, H(4) or H(5), 4H; 7.08, d, H(3), 4H, J(H(3,4) 8.13Hz); 2.28, s, Me, 6H.

Mass Spectrum (m/e, I%);

366 (M⁺, 17%), 365(16), 351(10), 288(18), 184(21), 193(62), 181(100), 169(95), 168(20), 154(15), 106(55), 104(27).

Osmometric Molecular Weight; Found 357, calc. 366.

Reaction of Phenylmethanes with Mercury(II) Iodide.

In a similar manner to dimer formation with lithiated (pyridin-2-yl)methanes, reaction of diphenyl- and triphenylmethane gave, respectively, 1,1,2,2-tetraphenylethane, (Ph₂HC)₂, from hexane, 16%, M.Pt. 212-213°, (lit. 213° ref. 11).

Infrared; 1598(w), 1582(w), 1494(m), 1450(m), 1158(m,br), 1072(m), 1030(m), 972(w), 742(s), 694(s), 608(s), 562(m).

¹H nmr (100 MHz); 7.07, m, Ph, 20H; 7.14, s, CH, 2H.

Mass Spectrum (m/e, I%); 334 (M⁺, 10%), 333(35), 168(18), 167(100), 166(10), 165(20).

Osmometric Molecular Weight; Found 325, calc. 334.

and

[Bis(triphenylmethyl)]peroxide,* (Ph₃CO)₂, from chloroform, 68%, M.Pt. 184-185°, (lit. 185° ref. 12).

Infrared; 1490(m), 1446(m), 1206(m), 1150(m,br), 1034(m), 974(m), 770(m), 754(s), 700(v.s.), 648(m), 634(m).

¹H nmr (100 MHz, CCl₄); 7.10, m, Ph, 30H.

* N.B. Reaction worked up under ambient conditions, i.e. oxygen present.

Mass Spectrum (m/e, I%); 259(Ph_3CO^+ , 60%), 243(18), 166(50), 165(100), 105(60).

Osmometric Molecular Weight; Insufficient solubility

The Reaction Between Lithiated 2-Benzylpyridine and *Trans*-[bis(4-methylpyridine)]palladium(II) chloride

To a stirred suspension of *trans*-[bis(4-methylpyridine)]palladium(II)chloride ($[(\gamma\text{-pic})_2\text{PdCl}_2]$, 4.168 g, 1.15 mmol.) in diethyl ether (150 cm^3) at -80°C was added lithiated 2-benzylpyridine (from 2-benzylpyridine 1.86 cm^3 , 1.16 mmol., and butyllithium 5.52 cm^3 , 2.3 M 1.27 mmol., in hexane) in THF (30 cm^3) dropwise over ca. 30 min. After gradual warming to room temperature benzene (100 cm^3) was added and the solution was heated to ca. 60° for 1h and most of the diethyl ether was removed by distillation.* After cooling, the deep red solution, containing some unreacted $[(\gamma\text{-pic})_2\text{PdCl}_2]$, was hydrolysed with water (40 cm^3) and the organic phase was isolated, filtered free of suspended solids, dried over magnesium sulfate, and reduced to dryness *in vacuo*. The resulting red/orange gum was extracted with hot hexane (80 cm^3) removing some free $\gamma\text{-pic}$, 2-benzylpyridine and dimerised 2-benzylpyridine. (The dimer $(\text{pyPhHC})_2$, (A), was isolated as colourless crystals on slow evaporation of the hexane solution (0.156 g)). The extracted gum was dissolved in dichloromethane (20 cm^3) and on addition of acetone (20 cm^3) and on slow evaporation (20h) gave orange crystals of (B) (1.412 g, 28%, M.Pt. $167-8^\circ$).

Product (A) was identified by comparison to a pure sample (see page 194, ^1H nmr and M.S. identification).

* The reaction may also be performed by suspending $[(\gamma\text{-pic})_2\text{PdCl}_2]$ in ether: benzene (1:1). Heating may then be avoided by extending the reaction period by ca. 4h.

Product (B)

Di[*trans*-(*N,N'*)-{(μ-pyridin-2-yl-*M*)(phenylmethyl-*C*)}(4-methylpyridine-*M*)palladium(II) chloride]. dichloromethane solvate.

[{(μ-py-*M*)(PhHC-*C*)}(γ-pic-*M*)PdCl]₂·CH₂Cl₂.

Analysis; Found (%), C 49.3, H 4.1, N 6.5, Cl 15.8.

Calc. (%), C 49.8, H 4.1, N 6.3, Cl 15.9.

Infrared; 1618(m), 1594(s), 1562(m), 1468(m), 1442(m), 1428(m), 1210(m), 1166(m), 1070(w), 1038(m), 972(w), 816(s), 772(s), 730(s), 702(m), 628(w), 606(w), 592(w), 500(s,br).

¹H nmr (300 MHz, -20°C) 9.20, d, γ-pic H(6), 2H, J(H(6,5) 6Hz); 9.01, d, py H(6), 1H, J(H(6,5) 5Hz); 8.07, d, Ph(6), 1H, J(H(6,5) 8Hz); 7.48, t, Ph(5), 1H, J(8Hz); 7.15-7.00, m, comprising γ-pic H(3,5), Ph(4), and py H(3,5), 5H; 6.88, t, py H(4), 1H, J(6Hz); 6.76, t, Ph(3), 1H, J(8Hz); 6.19, d, Ph(2), 1H, J(H(2,3) 8Hz); 5.92, s, CH, 1H; 2.33, s, CH₃, 3H.

see page 118 for ring assignments.

¹³C nmr (¹H decoupled, -20°C) 173.0, 151.9, 151.6, 151.0, 148.8, 143.0, 135.8, 128.4, 128.1, 127.8, 126.6, 126.1, 125.8, 124.2, 122.4, 118.6, 43.3, 20.9.

see page 119 for assignments.

Chromatographic separation of the crude product gives 2-benzylpyridine, γ-pic, and (pyPhCH)₂ (A) as the first eluents on a silica gel column under medium pressure with chloroform - 4% ethyl acetate elution. These are followed by a minor orange component (R_f. 0.70, same solvent) that has been crystallised from acetone/dichloromethane (*product C*, 4%, M.Pt. 215° dec.), and a major red fraction, (D) (R_f. 0.24, same solvent), that gives red crystals from acetone/dichloromethane (*product D*, 5%, M.Pt. 146-148°) (See pages 113-114 for structures and comment on reaction products.)

Product C

Trans-N,N'-bis[1-phenyl-1-(pyridin-2-yl)prop-1-en-2-olato]
palladium(II),
[{pyPhC:C(Me)O-N,O}₂Pd].

Analysis; Found (%), C 63.8, H 4.6, N 5.3.

Calc. (%), C 63.8, H 4.6, N 5.3.

Infrared; 1604(m), 1574(s), 1512(s), 1456(s,br), 1382(m),
 1276(m), 1166(m), 974(s), 746(m), 700(s), 654(m).

¹H nmr (300 MHz); 8.82, d, py H(6), 1H, J(H(6,5) 6Hz); 7.42, m,
 Ph(3,5), 2H; 7.33-7.25, m, comprising py H(5) and
 Ph(4), 2H; 7.21, d, Ph(2,6), 2H, J(7Hz); 6.76, t, py
 H(4), 1H, J(6 Hz); 6.41, d, py H(3), 1H, J(H(3,4) 8Hz);
 1.85, s, CH₃, 3H.

¹³C nmr (¹H decoupled); 167.4, 153.6, 146.4, 142.0, 136.1, 132.4,
 129.1, 126.5, 121.9, 115.0, 110.0, 25.0.

Mass Spectrum (m/e, I%); 527 (M⁺, ca. 10%, isotopic cluster of 7
 lines), 310 (10, isotopic), 211(20), 210(18), 196(14),
 194(13), 184(13), 180(25), 169(100), 168(90), 167(75).

Osmometric Molecular Weight; Found 530, calc. 527.

Product D

Analysis; Found (%), C 57.0, H 4.2, N 5.5, Cl 11.2^{*}

Calc. (%), C 56.9, H 4.3, N 6.1, Cl 9.3.^{*}

* Traces of occluded CH₂Cl₂ could not be satisfactorily
 removed.

Infrared; 1596(s,br), 1568(m), 1472(s,br), 1436(s,br), 1302(m),
 1156(m), 1074(m), 1030(m), 994(m), 812(m), 768(v.s.),
 744(v.s), 696(v.s), 650(m), 624(m), 602(w), 576(m),
 466(m), 448(m).

¹H nmr (300 MHz); Bridging (deprotonated) 2-benzylpyridine; 9.24,
 d, py H(6), 4H, J(H(6,5) 5.4Hz); 8.00, m, Ph H(6), 4H;
 7.56, m, Ph H(5), 4H; 7.34, *, Ph H(4), 4H; 7.16, *, py
 H(4), 4H; 6.93, m, py H(5), 4H; 6.90, Ph H(3), 4H;
 6.12, d, Ph H(2), 4H, J(H(2,3) 6.9Hz); 6.04, s, CH, 4H.

(py H(3) not identified but presumed to resonate within the region 7.6-7.1 ppm).

N-bound 2-benzylpyridine; 10.76, d, py H(6), 4H, J(H(6,5) 5.7Hz); 7.57, *, py H(4), 4H; 7.25, *, py H(3), 4H; 6.63, d, py H(3), 4H, J(H(3,4) 7.8Hz); 5.63, d, CH, 4H, J(17.4Hz, geminal); 3.43, d, CH, 4H, J(17.4Hz, geminal). (Individual phenyl proton resonances not identified but occur in the region 7.6-7.1 ppm) γ -picoline from " $(\gamma\text{-pic})_2\text{PdCl}_2$ "; 9.04, d, py H(6,2), 2H, J(H(6,5) 5.4Hz); 8.91, py H(6,2), 2H, J(H(6,5) 5.4Hz); 7.25, *, py H(5,3), 4H; 5.43, s, CH₃, 3H; 5.30, s, CH₃, 3H.

* Resonance position estimated from the COSY spectrum.

Di[Trans-(N,N')-(μ -pyridin-2-yl-N(phenylmethyl)-C)]
(2-benzylpyridine-N)palladium(II) chloride],
[(μ -py-N(PhHC-C))(pyPhCH₂-N)PdCl]₂.

To product B (0.572g, 0.64 mmol) was added a large excess of 2-benzylpyridine (0.5 cm³) and the mixture was warmed to 100° for 1h. All volatile components were then removed by slow distillation at 80-100° under vacuum (0.5 mm) until an orange crystalline solid remained. The solid was dissolved in dichloromethane (5 cm³), filtered and acetone (5 cm³) was added. The title complex crystallised as orange plates on enclosure in a sealed chamber with diethyl ether. (0.528g, 0.55 mmol, 86% M.Pt. 184-186° dec.).

Analysis; Found (%), C 59.75, H 4.41, N 5.77, Cl 8.00.

Calc. (%), C 60.14, H 4.42, N 5.84, Cl 7.40.

Infrared; 1598(s), 1568(m), 1488(m), 1468(s), 1450(m), 1428(m), 1418(m), 1160(m), 772(s), 764(m), 742(s), 704(s), 626(m), 604(m), 470(m), 448(m).

¹H nmr (300 MHz);

Bridging (deprotonated) 2-benzylpyridine; 9.24, d, py H(6), 2H, J(H(6,5) 5.4Hz); 8.02, d, 2H, Ph H(6), J(H(6,5) 6.7Hz); 7.55, m, Ph H(5), 2H; 7.34, *, Ph H(4), 2H; 7.16, *, py H(4), 2H; 6.94, *, py H(5), 2H; 6.93, *, Ph H(3), 2H; 6.18, d, Ph H(2), 2H, J(H(2,3)

7.5Hz); 6.14, s, CH. (py H(3) not identified but presumed to resonate within the region 7.36-7.10 ppm). N-bound 2-benzylpyridine; 10.77, d, py H(6), 2H, J(H(6,5) 4.5Hz) 7.56, m, py H(4), 2H; 7.24, *, py H(5), 2H; 6.63, d, py (H(3), 2H, J(H(3,4) 8.1Hz); 5.71, d, CH, 2H, J(17.1Hz, geminal); 3.56, d, CH, 2H, J(17.1Hz, geminal). (Individual phenyl proton resonances not identified but occur in the region 7.36-7.05 ppm).

* Resonance position estimated from the COSY spectrum.

Osmometric Molecular Weight; Found 1004, calc. 959.

Oxidative Addition Reactions with Bis(dibenzylideneacetone) palladium(0).

The oxidative addition of $\text{py}_n\text{Ph}_{3-n}\text{CCl}$ ($n = 1,2,3$) to $[(\text{dba})_2\text{Pd}]$ is described for $n=2$. Reactions for $n = 1,3$ were carried out under similar conditions. No oxidative addition products were isolated for $n=3$ (see page 149).

Di[trans-(N,N')-(μ-pyridin-2-yl-M)(pyridin-2-yl-M)(phenylmethane-C)]palladium(II) chloride]. acetone, dichloromethane solvate,
 $[(\mu\text{-py-M})(\text{py-M})(\text{PhC-C})\text{PdCl}]_2 \cdot [(\text{CH}_3)_2\text{CO} \cdot \text{CH}_2\text{Cl}_2]_{0.5}$

Under anaerobic anhydrous conditions $[(\text{dba})_2\text{Pd}]$ (0.814g, 1.43 mmol) was suspended in benzene (150 cm³) with stirring. The solid ligand, py_2PhCCl , (0.401g, 1.43 mmol) was added and the solution was allowed to stir for 20h. Under atmospheric conditions the resulting deep red solution was filtered free of suspended solids and the filtrate was reduced to dryness giving a deep red-brown residue. The residue was separated by chromatography (medium pressure, silica gel, chloroform elution) giving a deep red eluent (R_f 0.14) after prior elution of some free dba and $[(\text{dba})_3(\text{CHCl}_3)\text{Pd}_2]^*$. Reduction of the red eluent to dryness gave a deep magenta solid which was recrystallised by dissolution in a small volume of CH_2Cl_2 and addition of acetone (0.253g, 39%,

* $"[(\text{dba})_2\text{Pd}]" + \text{CHCl}_3 \rightarrow [(\text{dba})_3(\text{CHCl}_3)\text{Pd}_2] + \text{dba}.$

M.Pt. 245-247° dec.). Crystals suitable for X-ray study were obtained by dissolution of a sample in CH_2Cl_2 , addition of an equivalent volume of acetone, and addition of diethyl ether by vapour diffusion in a sealed chamber. (Transparent magenta crystals were obtained that gradually became opaque on storage for more than one week.)

Analysis; Found (%), C 50.72, H 3.89, N 6.60, Cl 10.9.

Calc. (%), C 51.12, H 3.57, N 6.62, Cl 12.57.

(N.B. complete removal of solvent molecules, CH_2Cl_2 and acetone, was not possible. X-ray analysis (see page 140) indicates half a molecule of CH_2Cl_2 and acetone per Pd dimer, and gradual change in solvate composition has been noted using ^1H nmr).

Solvate; CH_2Cl_2 , detection; ^1H nmr. Acetone, detection; ^1H nmr and I.R.

Infrared; 1708(m) (C=O), 1592(m), 1466(s), 1442(m), 1168(s), 1032(m), 974(m), 934(w), 794(w), 758(m), 722(s), 678(m), 644(m).

^1H nmr (300 MHz)*; 8.53, m, H_B^6 , 2H, $J(\text{H}_\text{B}^6, ^5\text{H}_\text{B}^5) 4.3\text{Hz}$; 8.12, m, H_C^6 , 2H, $J(\text{H}_\text{C}^6, ^5\text{H}_\text{C}^5) 5.7\text{Hz}$; 7.82, td, H_B^4 , 2H, $J(\text{H}_\text{B}^4, ^3\text{H}_\text{B}^3) = \text{H}_\text{B}^4, ^5\text{H}_\text{B}^5 7.9\text{Hz}$, $\text{H}_\text{B}^4, ^6\text{H}_\text{B}^6 = 1.7\text{Hz}$; 7.43, td, H_C^4 , 2H, $J(\text{H}_\text{C}^4, ^3\text{H}_\text{C}^3) = \text{H}_\text{C}^4, ^5\text{H}_\text{C}^5 7.7\text{Hz}$, $\text{H}_\text{C}^4, ^6\text{H}_\text{C}^6 = 1.7\text{Hz}$; 7.37-7.26, m, comprising H_B^5 , H_C^3 , H(5), 6H; 7.18, tt, H(4), 2H, $J(\text{H}(4,3)=\text{H}(4,5) 7.4\text{Hz}$, $\text{H}(4,2)=\text{H}(4,6) 0.9\text{Hz}$; 7.06-7.01, m, comprising H_C^5 , H(3), 4H; 6.82, d(br.), H(6), 2H, $J(\text{H}(6,5) 8.0\text{Hz}$; 6.65, dt, H_C^3 , 2H, $J(\text{H}_\text{C}^3, ^4\text{H}_\text{C}^4) 8\text{Hz}$, $\text{H}_\text{C}^3, ^5\text{H}_\text{C}^5 = \text{H}_\text{C}^3, ^6\text{H}_\text{C}^6 1.0\text{Hz}$; 6.13, d(br), H(2), 2H, $J(\text{H}(2,3) 7.9\text{Hz}$.

^{13}C nmr (^1H -decoupled)*; 171.31, 168.54, 154.08, 146.00, 145.26, 138.72, 136.03, 129.53, 128.50, 128.26, 126.59, 125.30, 124.14, 123.77, 123.21, 122.70, 25.88.

* For method of assignment of COSY and ^{13}C spectra see pages 144-148

Di[η^3 - α -(phenyl)- α -(pyridin-2-yl)toluene]palladium(II) chloride]
[η^3 -(pyPh₂C)PdCl]₂.

In a similar manner to the above pyPh₂CCl was reacted with [(dba)₂Pd]. Chromatographic separation (medium pressure, silica gel, chloroform elution) gave the product as an orange band (*R_f* 0.14). On removal of solvent and addition of acetone the product separated out as orange micro-crystals (22%, M.Pt. 154-6° dec.). The orange band is closely followed by a red fraction that has not been fully characterised.

Analysis; Found (%), C 55.78, H 3.71, N 3.59, Cl 8.7

Calc. (%), C 55.99, H 3.65, N 3.68, Cl 9.2.

Infrared; 1592(m), 1490(w), 1462(m), 1436(m), 1384(m,br), 1152(m), 1032(w), 974(w), 770(w), 758(m), 730(s), 698(s), 648(m), 612(m).

¹H nmr (300 MHz); 8.21, d(br), H_A⁶, 1.4H, J(H_A^{6,5} ca. 5Hz); 8.09, d(br) H_B⁶, 0.6H, J(H_B^{6,5} ca. 5Hz); 7.74, t(br), H_{A,B}⁴, 2H, J(H_{A,B}^{4,3} and/or H_{A,B}^{4,5} ca. 8Hz); 7.59, d(br), phenyl(ortho)_B, 2.4H, J(H(ortho-meta) ca. 7Hz); 7.50, d(br), phenyl(ortho)_A, 5.6H, J(H(ortho-meta) ca. 7Hz); 7.28-7.13, m, comprising H_{A,B}⁵ and phenyl(meta, para)_{A,B}, 14H; 6.87, d(br), H_{A,B}³, 2H, J(H_{A,B}^{3,4} ca. 8Hz).

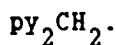
¹³C nmr (¹H-decoupled) 174.0(q), 145.5(q), 143.8(q), 138.1(q), 129.5, 129.0, 128.2, 125.6, 122.8, 122.0,

See pages 130 and 138 for nmr assignments.

Osmometric Molecular Weight; Found, 760, calc., 772.

(Pyridin-2-yl)methane Ligands and Derivatives.

Bis(pyridin-2-yl)methane, *



Bis(pyridin-2-yl)methanone (5.0g, 2.7 mmol) was added to a solution of potassium hydroxide (3.14g, 5.6 mmol) in diethylene glycol (100 cm³), giving a dark red solution. Hydrazine hydrate (3.0 cm³, 6.2 mmol) was added, resulting in reflux, and the solution was further refluxed for 4h to give a transparent orange solution. On cooling, water (100 cm³) was added, and the solution was extracted with benzene (6 x 30 cm³). The extracts were dried over magnesium sulfate, evaporated under reduced pressure, and distilled. The initial fraction, which is pale yellow and boils at 78-100°/0.1 mm, was collected, and a solution of the dihydrobromide salt prepared by the addition of 46-48% hydrobromic acid (4.2 cm³) to this fraction. On dilution with ethanol (100 cm³) and standing colourless crystals formed and were collected. A further crop was obtained from the filtrate on volume reduction (to ca. 30 cm³) by heating, followed by cooling and addition of diethyl ether (ca. 100 cm³). The crops were combined and dissolved in water (ca. 50 cm³), neutralized with potassium carbonate, extracted with chloroform (8 x 10 cm³), and the combined extracts dried over magnesium sulfate. The solution was evaporated under reduced pressure and distilled to give bis(pyridin-2-yl)methane as a colourless liquid (2.31g, 50%), b.p. 73-78°/0.1 mm (lit. 106-111°/0.5 mm, ref. 13). The distillation residue contains traces of the dimer (py₂CH)₂ (ca. 1-2%) as a colourless crystalline solid.

¹H nmr (100 MHz); 8.58, d, H(6), 2H, J(H(6,5) 5Hz); 7.65, m, H(3), 2H; 7.40-7.07, m, H(4,5), 4H, 4.37, s, CH₂, 2H.

The ligands py_nPh_{3-n}CH (n = 1-3) may all be prepared by a similar route. The member pyPh₂CH is commercially available

* Bis(pyridin-2-yl)methane may be prepared in 80% yield by Wolff-Kishner reduction of bis(pyridin-2-yl)methanone with hydrazine and base in a bomb at 150°C.¹⁴

(Aldrich).

Preparation of py_2PhCH , and a byproduct of the reaction, py_3PhC , is detailed below. Preparation of py_3CH is reported elsewhere¹⁵ and its synthesis for this work has been carried out without modification.

α,α -Bis(pyridin-2-yl)toluene,

py_2PhCH .

A deep red solution was obtained on addition of 2-benzylpyridine (14 cm^3 , 93.5 mmol) to a solution of phenyllithium [from lithium (1.292g, 186.2 mmol) and bromobenzene (9.85 cm^3 , 93.5 mmol)] in diethyl ether (100 cm^3). After stirring for 20 min, 2-bromopyridine (9.1 cm^3 , 93.3 mmol) in diethyl ether (20 cm^3) was added dropwise followed by addition of toluene (200 cm^3). On reflux most of the ether was removed by distillation, and reflux was continued for 12h to give a dark red-brown solution. On cooling, water (30 cm^3) was added and 5M HCl added until the aqueous phase became acidic to litmus. The aqueous extract was combined with an aqueous wash from the organic phase and made alkaline by addition of a saturated sodium bicarbonate solution. A chloroform ($3 \times 50\text{ cm}^3$) extract was dried with magnesium sulfate, filtered, and removal of solvent in a vacuum gave a brown oil containing some crystals. The oil was dissolved in cold ethanol, and the sparingly soluble crystals were collected and recrystallised from hot benzene after treatment with activated charcoal, to give colourless crystals of α,α,α -tris(pyridin-2-yl)toluene, py_3PhC , (2.067g, 6.40 mmol, 7%, M.Pt. sub. 220°). The ethanol solution was reduced to an oil under vacuum, and the oil was extracted with petroleum ether ($3 \times 50\text{ cm}^3$) with the inclusion of activated charcoal. The filtrate from the extraction gave an initial crop of α,α -bis(pyridin-2-yl)toluene, py_2PhCH as almost colourless crystals (1.793g, 7.29 mmol, 8%). Further crops (totalling 4.80g) were discoloured by a yellow contaminant. Chromatography on a short silica column with chloroform elution gave py_2PhCH (R_f 0.5, 4.26g, 18%) after prior elution of the yellow contaminant.

The title ligand, py_2PhCH , had identical spectral and physical characteristics to those reported. Characteristics of the byproduct are summarized below.

py_3PhC

Analysis; Found (%), C 81.1, H 5.1, N 13.3.

Calc. (%), C 81.7, H 5.3, N 13.0.

Infrared; 1586(m), 1564(m), 1464(s), 1442(s), 1150(w), 992(w), 780(m), 740(s), 704(m), 662(m), 642(w), 618(m).

^1H nmr (100 MHz); 8.84, d, H(6), 3H, J(H(6,5) 5Hz); 7.60-6.90, m, H(3-5) and Ph, 14H.

Mass Spectrum (m/e, I%); 323 (M^+ , 11%), 322(15), 246(5), 245(100), 244(73), 243(33), 167(50).

^1H nmr reference compounds of the type $\text{py}_n\text{Ph}_{3-n}\text{CMe}$ ($n = 1-3$) have been prepared from the ligands $\text{py}_n\text{Ph}_{3-n}\text{CH}$. For $n = 2, 3$, the products were highly crystalline. However, for $n = 1$, the product formed as a very viscous oil and has only been characterized by ^1H nmr and M.S. The details for py_2PhCMe ($n = 2$) are given below. Preparations for $n = 1$ and 3 are similar.

α -Methyl- α , α -bis(pyridin-2-yl)toluene,

py_2PhCMe .

To an ether solution of methyllithium containing excess methyl iodide [from lithium (0.205g, 29.5 mmol) and methyl iodide (1.87 ml, 30.0 mmol) in ether (60 cm^3)] was added py_2PhCH (3.453g, 14.0 mmol) in ether (30 cm^3) at -15° . The solution was allowed to stir at ambient temperature for 5h, then hydrolysed with water (30 cm^3), and conc. HCl was added until the aqueous phase became acidic to litmus. The acidic aqueous phase was isolated, neutralised with saturated sodium carbonate solution, and extracted with dichloromethane (3 x 30 cm^3). The dichloromethane extract was dried with magnesium sulfate, filtered, and taken to dryness giving the crude product as a viscous pale tan oil. Addition of hot petroleum-ether (40-60) and slow cooling gave the product as a crystalline solid. Recrystallisation from petroleum-ether with the inclusion of activated charcoal gave the pure product as large colourless crystals (2.893g, 11.1 mmol, 80%, M.Pt. $63-65^\circ$).

Analysis; Found (%), C 83.16, H 6.25, N 10.90.

Calc. (%), C 83.04, H 6.20, N 10.76.

^1H nmr (100 MHz); 8.56, d, H(6), 2H, J(H(6,5) 5Hz); 7.60-6.95, m, H(3-5) and Ph, 11H; 2.27, s, CH_3 , 3H.

Mass Spectrum (m/e, I%) 260 (M^+ , 35%), 259(32), 245(70), 244(25), 182(50), 181(100), 180(50), 167(50), 123(30).

1,1,1-Tris(pyridin-2-yl)ethane,

py_3CMe .

As above, from benzene/petroleum-ether (40-60) (68%, M.Pt. 74-75°).

Analysis; Found (%), C 78.03, H 5.62, N 16.15.

Calc. (%), C 78.13, H 5.79, N 16.08.

^1H nmr (100 MHz); 8.55, d, H(6), 3H, J(H(6,5) 6Hz); 7.60-7.35, m, H(4), 3H; 7.15-6.95, m, H(3) and H(5), 6H; 2.27, s, CH_3 , 3H.

Mass Spectrum (m/e, I%) 261, (M^+ , 10%), 260(8), 247(12), 246(80), 184(15), 183(100), 182(12), 181(14), 168(20).

α -Methyl- α -phenyl- α -(pyridin-2-yl)toluene,

pyPh_2CMe .

As above, giving viscous colourless oil from petroleum-ether (40-60) (80%).

^1H nmr (100 MHz); 8.56, m, H(6), 1H; 7.50-6.85, m, 13H; 2.20, s, CH_3 , 3H.

Mass Spectrum (m/e, I%) 259 (M^+ , 90%), 258(100), 244(25), 243(45), 167(40).

Ligands of the general type $\text{py}_n\text{Ph}_{3-n}\text{CCl}$ ($n = 1-3$) have all been prepared here from the previously reported methanols $\text{py}_n\text{Ph}_{3-n}\text{COH}$.¹⁷ (The methanols have been prepared without modification to the methods reported).

Full details of the preparation of py_2PhCCl and pyPh_2CCl are given below. Preparation of py_3CCl has been slightly modified compared with that given in the literature¹⁸ and only the modifications have been noted.

α -Chloro- α , α -bis(pyridin-2-yl)toluene,
py₂PhCCl

Under anhydrous conditions py₂PhCOH (7.655g, 29.2 mmol) dissolved in THF (60 cm³) was treated with NaH (1.379g, 56% dispersion in mineral oil, 32.2 mmol) and the solution was stirred until no further evolution of H₂ was observed (ca. 1h). The solution was then chilled to 0°C and SOCl₂ (2.34 cm³, 32.1 mmol) in THF (10 cm³) was added slowly dropwise. After stirring for a further hour the solution was hydrolysed with water (20 cm³) and the organic phase was isolated, dried over magnesium sulfate, filtered, and taken to dryness giving a tan oil that rapidly crystallised. The crude product was recrystallised twice from CH₂Cl₂/petroleum-ether (40-60) giving the product as colourless crystals (6.05g, 21.6 mmol, 74%, M.Pt. 92-93°).

Analysis; Found (%), C 72.87, H 4.40, N 10.03, Cl 12.7.

Calc. (%), C 72.73, H 4.67, N 9.98, Cl 12.6.

Infrared; 1582 (m,br), 1462(m), 1432(m), 1152(m), 1052(m), 990(m), 858(m), 768(s), 742(v.s, br) 698(s), 654(m), 634(m), 614(s).

¹H nmr (100 MHz) 8.59, d, H(6), 2H, J(H(6,5) 4Hz); 7.80-7.10, m, H(3-5) and Ph, 11H.

Mass Spectrum (m/e, I%); 280 (M⁺, ca. 1%)*, 246(80), 245(100), 244(35), 169(43), 168(40), 167(45).

α -Chloro- α -phenyl- α -(pyridin-2-yl)toluene,
pyPh₂CCl¹⁹.

After reaction of pyPh₂COH with NaH and SOCl₂, as above, the THF solution was taken to dryness under vacuum giving a colourless gum. The gum was extracted with boiling petrol three times and, on filtration and volume reduction, the product was obtained on cooling as colourless dendritic crystals (34%, M.Pt. 65-67° lit. 72.2-73.2°, ref. 19).

* Only that isotope fraction containing ³⁵Cl was observed. Ammonia chemical ionisation shows an isotope cluster at 283 (MH⁺) and 281 (MH⁺) containing ³⁷Cl and ³⁵Cl, respectively.

N.B. The product is hydrolysed by water to pyPh_2COH .

Infrared; 3060(m), 1584(m), 1494(m), 1462(m), 1446(s), 1430(s), 1132(m), 1032(m), 896(m), 832(m), 774(s), 758(s), 746(v.s), 696(v.s), 614(m).

^1H nmr (100 MHz); 8.58, d, H(6), 1H, J(H(6,5) 5Hz); 7.60-7.00, m, H(3-5) and Ph, 13H.

Mass Spectrum (m/e, I%); 279 (M^+ , ca. 1%)*, 245(70), 244(100), 167(25), 165(20).

Chlorotris(pyridin-2-yl)methane,

py_3CCl .

Prepared by the method given by Faller and White,¹⁸ but at 0°C. Any highly coloured impurities may be readily removed by treating the acetone solution used in recrystallisation with activated charcoal. The yield is unaffected.

Extended Ligands Containing Two Bridging Carbon Atoms.

2,6-Bis[1,1-(pyridin-2-yl)ethyl]pyridine,

$(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}$.

A deep-red solution containing an orange solid was obtained on addition of bis(pyridin-2-yl)methane (9.906g, 58.3 mmol) in diethyl ether (60 cm³) to a solution of phenyllithium (from Li, 130.4 mmol, and bromobenzene, 260 mmol) in diethyl ether (200 cm³) at 0°C. After stirring for 20 min iodomethane (3.65 cm³, 58.6 mmol) in diethyl ether (20 cm³) was added to the chilled solution, resulting in rapid discharge of the solution colour. On allowing the solution to warm to ambient temperature, and stirring for a further 1.5h, water (20 cm³) was added and 5M HCl added until the aqueous phase became acidic to litmus. The isolated aqueous extract was washed once with dichloromethane (20 cm³), and made alkaline by addition of a saturated sodium bicarbonate solution. The crude product, py_2MeCH , was extracted

* Ammonia chemical ionisation shows the parent ions at 282 (MH^+) and 280 (MH^+) containing ^{37}Cl and ^{35}Cl , respectively.

with dichloromethane ($3 \times 50 \text{ cm}^3$), dried over magnesium sulfate, filtered, and the solvent removed by rotary evaporation to give a red oil. Vacuum distillation, with isolation of the fraction boiling at $84-102^\circ$ (0.15 mm) gave py_2MeCH as a colourless oil (8.80g, 47.8 mmol, 82%).

A deep-red solution was obtained on addition of py_2MeCH (2.987g, 16.2 mmol) in diethyl ether (30 cm^3) to a chilled solution of phenyllithium (as above, using 36.9 mmol lithium) in diethyl ether (100 cm^3). After stirring for 20 min., 2,6-dichloropyridine (1.205g, 8.1 mmol) in diethyl ether (30 cm^3) was added rapidly dropwise, partially discharging the solution colour and precipitating an orange solid. Toluene (120 cm^3) was added, diethyl ether was removed by distillation, and the resulting suspension was refluxed for 12h. Hydrolysis and extraction (as above) gave a yellow oil that rapidly crystallised. The crude product, $(\text{py}_2\text{MeC})_2\text{C}_5\text{H}_3\text{N}$, was washed with cold acetone (5 cm^3), and recrystallised from hot acetone after treatment with activated charcoal giving colourless crystals (1.404g, 3.17 mmol, 39%, M.Pt. $134-136^\circ$).

After isolation of the desired product a considerable oily residue remained. On removal of py_2MeCH by distillation, a less volatile fraction remained. Dissolution of the residue in hot petrol, treatment with activated charcoal, filtration and cooling yielded a near colourless viscous oil. The oil could not be induced to crystallise but spectral evidence (M.S., ^1H nmr) indicated the monosubstitution product, $(\text{py}_2\text{MeC})\text{C}_5\text{H}_3\text{NCl}$.

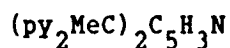
py_2MeCH

Analysis; Although the product was apparently pure by ^1H nmr, satisfactory microanalysis could not be obtained, possibly due to the hygroscopic nature of the liquid.

Infrared; (thin film) 3052(m), 3004(m), 2972(m), 2932(m), 1588(v.s), 1570(v.s), 1472(v.s), 1434(v.s), 1372(m), 1284(m), 1194(m), 1150(s), 1042(s), 994(s), 890(m), 818(s), 754(v.s.br), 630(s), 616(s), 550(s).

^1H nmr (100 MHz); 8.52, d, H(6), 2H, J(H(6.5) 5Hz); 7.65-7.00, m, H(3-5), 6H; 4.42, q, CH, 1H, J((CHCH₃) 7Hz); 1.74, d, CH₃, 3H, (J(CHCH₃) 7Hz).

Mass Spectrum (m/e, I%); 184 (M^+ , 15%), 183(27), 182(13), 170(24), 169(100), 168(24), 106(50).



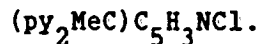
Analysis; Found (%), C 83.9, H 6.3, N 9.4.

Calc. (%), C 84.3, H 6.2, N 9.5.

Infrared; 1584(s), 1464(s), 1452(s), 1366(m), 1292(m), 1152(m), 1046(m), 992(m), 788(m), 754(s), 614(m), 584(m).

¹H nmr (300 MHz); 8.52, m, H(6), 4H, J(H(6,5) 4.8Hz); 7.56, m, H(4, central ring), 1H; 7.41, m, H(5 or 4 terminal ring), 4H; 7.05, m, H(4 or 5 terminal ring) and H(3 and 5, central ring), 6H; 6.86, m, H(3, terminal ring); 2.21, s, CH₃, 6H.

Mass Spectrum (m/e, I%); 443 (M^+ , 20%), 429(25), 428(50), 414(43), 366(12), 365(30), 350(37), 280(36), 261(15), 260(39), 245(15), 184(21), 183(100), 182(21), 169(46), 168(30).

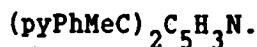


Infrared; (Thin film); 3088(m), 3056(m), 1582(v.s.,br), 1470(s), 1430(v.s), 1400(s), 1162(s), 1138(s), 990(s), 878(m), 792(s), 748(s), 684(s), 618(m).

¹H nmr (100 MHz); 8.56, d, H(6), 2H, J(H(6,5) 5Hz); 7.70-6.95, m, H(3-5), 9H; 2.30, s, CH₃, 3H.

Mass Spectrum (m/e, I%); 297 and 295 (M^+ , 6%, 16%, resp.), 280(60), 217(55), 183(100).

2,6-Bis[1-(phenyl)-1-(pyridin-2-yl)ethyl]pyridine,



In a similar manner to the preparation of (py₂MeC)₂C₅H₃N, the title ligand was prepared from lithiated 2-(1-phenylethyl)pyridine, pyPhMeCH (95% from 2-benzylpyridine, B.Pt. 88-94°/0.1mm), and 2,6-dichloropyridine, giving the product as colourless crystals from ether/hexane (32%, M.Pt. 96-97°).



Analysis; Found (%), C 85.1, H 7.1, N 7.5.

Calc. (%), C 85.2, H 7.1, N 7.6.

Infrared; (Thin film); 1590(s), 1570(s), 1496(s), 1474(s), 1454(s), 1434(s), 1148(m), 1084(m), 1046(m), 1028(m), 806(m), 748(s), 700(s), 640(m), 610(m), 586(m).

¹H nmr (100 MHz); 8.53, d, H(6), 1H, J(H(6,5) 5Hz); 7.60-6.90, m, H(3-5) and Ph, 8H; 4.24, q, CH, 1H, J((CHCH₃) 7.5Hz); 1.65, d, CH₃, 3H, J((CHCH₃) 7.5Hz).

Mass Spectrum (m/e, I%); 183 (M⁺, 50%), 182(100), 168(36), 167(53), 106(25).

(pyPhMeC)₂C₅H₃N.

Analysis; Found (%), C 83.9, H 6.3, N 9.4.

Calc. (%), C 84.3, H 6.2, N 9.5.

Infrared; 1574 (s,br), 1494(m), 1470(s), 1444(s), 1428(s), 1152(m), 1080(w), 1066(m), 1026(m), 992(m), 772(m), 762(s), 728(s), 630(m).

¹H nmr (300 MHz); 8.54, m, H(6), 2H, J(H(6,5) 4Hz); 7.50, m, H(4) central ring, 1H; 7.39, m, 2H; 7.23-7.14, m, 6H; 7.07-6.97, m, 8H; 6.88, m, 2H; 2.15, s, Me, 6H.

Mass Spectrum (m/e, I%); 441 (M⁺, 35%), 426(100), 260(52), 259(42), 183(44), 182(92), 181(33), 180(35), 168(24), 167(92).

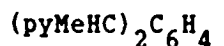
1,3-Bis[1-(pyridin-2-yl)ethyl]benzene,
(pyMeHC)₂C₆H₄.

To a chilled (-50°) solution of phenyllithium (from Li, 142 mmol, and bromobenzene, 64.3 mmol) in ether (100 cm^3) was added 2-bromopyridine (6.27 cm^3 , 64.3 mmol) in ether (30 cm^3) and the solution was allowed to stir for 30 min. To the deep red solution of 2-lithiopyridine was added 1,3-diacetylbenzene (4.735g, 29.2 mmol) in ether (30 cm^3) over a 15 min. period producing a thick purple slurry. After allowing the solution to warm to room temperature over ca. 2h the solution was hydrolysed with water (50 cm^3) and worked up in the usual manner (e.g. see page 205), by acid extraction, giving the crude alcohol *1,3-bis[1-hydroxy-1-(pyridin-2-yl)ethyl]benzene* (7.88g, ca. 84%) as a viscous brown oil after drying under vacuum (3h, 70° , 0.1mm).

The crude alcohol was dehydrated by dissolution in a mixture of glacial acetic acid and concentrated sulphuric acid (50 and 100 cm^3 , resp.) and standing for 24h. After neutralisation of the solution by the addition of saturated sodium carbonate solution the crude alkene, *1,3-bis[1-(pyridin-2-yl)ethenyl]benzene*, separated as brown oily droplets and was extracted into chloroform ($4 \times 50\text{ cm}^3$). On drying of the extract over magnesium sulfate and removal of solvent under vacuum the crude alkene was obtained as a very dark oil. Low R_f material was removed by elution through a short silica column ($\text{CHCl}_3/\text{MeOH}$ - 5%, medium pressure) with the desired product isolated as the first eluent (R_f 0.25, CHCl_3) prior to a red/purple band, yielding 4.637g (ca. 66%), of the alkene.

The alkene was quantitatively hydrogenated (^1H nmr) in ethyl acetate (80 cm^3) over 4h with hydrogen (60 psi) using 5% palladium on charcoal catalyst. The product, *1,3-bis[1-(pyridin-2-yl)ethyl]benzene*, was then distilled under vacuum (B.Pt. $140-2^{\circ}$, 0.02 mm) giving a very pale yellow viscous oil.*

* Due to the nature of the product microanalysis has not been attempted. However a cyclometallation product of this ligand has been prepared and satisfactorily analysed (see page 188).

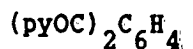


Infrared; (Thin film); 3136(s), 3052(s), 3004(s), 2968(s), 2928(s), 1590(v.s), 1570(s), 1486(v.s), 1452(v.s), 1370(s), 1148(s), 1044(s), 994(s), 892(s,br), 782(s), 748(v.s), 706(v.s).

¹H nmr (300 MHz); 8.54, dd, (J(5,6) 5.6Hz, J(4,6) 1.8Hz), H(6), 2H; 7.54, m, 2H; 7.26-7.19, m, 3H; 7.13-7.05, m, 5H; 4.26, q, (J(CHCH₃) 7.3Hz), CH, 2H; 1.67, d, (J(CHCH₃) 7.3Hz), CH₃ 6H.

Mass Spectrum (m/e, I%) 289 (M +1⁺, 18%), 288 (M⁺, 4%), 287(10), 183(15), 182(100), 181(20), 180(45), 167(88), 106(35).

Ozonolysis of the alkene intermediate in ethylacetate at -50°C (1% wt/vol) yields the ketone *1,3-bis(pyridin-2-yl)methanonylbenzene* (92%, M.Pt. 114-115°), after reduction of the ozonide with dimethylsulfide, as a colourless crystalline solid from acetone.*



Analysis; Found (%), C 74.77, H 4.18, N 9.65.

Calc. (%), C 74.99, H 4.20, N 9.72.

¹H nmr (300 MHz); 8.82, m, Ph H(2), 1H, J(H(2,4) = H(2,6) 1.6 Hz); 8.73, m, py H(6), 2H, J(H(6,5) 4.8Hz); 8.35, dd, py H(3), 2H, J(H(3,4) 7.8Hz, H(3,5) 1.8Hz); 8.09, m, Ph H(4,6), 2H, J(H(4/6,5) 7.8Hz, H(4/6,2) 1Hz); 7.92, td, py H(4), 2H, J(H(4,3) = H(4,5) 7.7Hz, H(4,6) 1.8Hz); 7.64, t, Ph H(5), 1H, J(H(5,4/6) 7.7Hz); 7.51, ddd, py H(5), 2H, J(H(5,4) 7.6Hz, H(5,6) 4.8Hz, H(5,3) 1.3Hz).

Infrared; 1668(v.s), 1596(m), 1582(m), 1568(m), 1432(m), 1302(s), 1280(m), 1242(m), 1120(s), 1012(s), 826(m), 786(m), 738(s), 694(v.s), 662(s), 618(m).

Mass Spectrum (m/e, I%) 288 (M⁺, 12%), 287(7), 286(10), 285(8), 210(15), 182(100), 180(30).

* A metallation product containing this ligand has been the subject of X-ray structural analysis and is shown on page 79.

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 - 5) Interaction of Palladium(II) with Polydentate Ligands,
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Appendix 1 has been removed
for copyright or proprietary
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It has been published as: Canty, A. J.,
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acta, 102(2), L29-30

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It has been published as: Canty, A. J., Minchin, N. J., Skelton, B. W., White, A. H., 1986. Synthesis of the tridentate pyridine donor 2,6-bis[1-phenyl-1-(pyridin-2-yl)ethyl]pyridine (L), including separation of meso and rac diastereoisomers via methylmercury(II) derivatives, and an X-ray structural study of [HgMe(meso-L)]NO₃ 2H₂O, Journal of the Chemical Society, Dalton transactions, 10, 2201-2204

Appendix 4 has been removed
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It has been published as: Canty, A. J.,
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Appendix 5 has been removed
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It has been published as: Canty, A. J.,
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